

## PREFACE

This quarterly report presents current information on the timber situation in Alaska, Washington, Oregon, California, Montana, Idaho, and British Columbia, including data on lumber and plywood production and prices; timber harvest; employment in forest products industries; international trade in logs, pulpwood, chips, lumber, and plywood; log prices in the Pacific Northwest; volume and average prices of stumpage sold by public agencies; and other related items.

Historical data for the years before 1969 are in the 1979 issues of "Production, Prices, Employment, and Trade in Northwest Forest Industries."

Cooperation in supplying data has been received from a number of sources. These include the U.S. Department of Agriculture, Forest Service, Forest Resources Economics Research Staff in Washington, D.C.; Washington State Department of Natural Resources and Employment Security Department; Oregon State Department of Forestry and Department of Employment; California State Department of Employment and Department of Conservation; Montana State Forester and State Employment Service; Idaho State Department of Public Lands and Department of Employment; Alaska State Department of Labor and Department of Natural Resources of the Division of Lands; U.S. Department of Commerce; U.S. Department of the Interior, Bureau of Land Management and Bureau of Indian Affairs; British Columbia Department of Industrial Development, Trade, and Commerce; and a number of private industry associations, firms, and individuals.

The statistical data are from secondary sources and are brought together to make such information more readily available. Sources are indicated for each table and can be contacted directly for means used in data collection.

**KEYWORDS:** Forestry business economics, lumber, plywood, timber volume, stumpage sales, employment, marketing, log exports.

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TABLES INCLUDED IN THIS SERIES OF REPORTS, FREQUENCY OF PUBLICATION,  
AND MOST RECENT QUARTER PUBLISHED

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TIMBER HARVEST		
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<sup>1/</sup>A: Published annually as data become available.  
 B: Published biannually as data become available.  
 P: Published periodically as data become available.  
 Q: Published quarterly as data become available.



Montana and Idaho timber harvest by ownership, 1969-79	A	Third quarter 1980
British Columbia timber harvest, 1969-79	A	Third quarter 1980
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#### LUMBER AND PLYWOOD EXPORTS

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Douglas-fir Sawmill log prices, western Washington and northwestern Oregon, 1969-79	A	Second quarter 1980
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Noble fir log prices, western Washington and northwestern Oregon, 1969-79	A	Second quarter 1980
White fir log prices, western Washington and northwestern Oregon, 1969-79	A	Second quarter 1980
Sitka spruce log prices, western Washington and northwestern Oregon, 1969-79	A	Second quarter 1980
Western redcedar log prices, western Washington and northwestern Oregon, 1969-79	A	Second quarter 1980
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<u>Table title</u>	<u>Frequency</u>	<u>1950 Second quarter</u>
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Uncut volume under contract on National Forest lands in California, Montana, Idaho, Oregon, and Washington, 1969-79	A	Second quarter 1980
Allowable annual cut and uncut volume under contract on Bureau of Indian Affairs lands in Washington and Oregon, 1963-71	P	Fourth quarter 1971
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YEAR	TOTAL SOFTWOOD LUMBER	WESTERN WASHINGTON AND WESTERN OREGON	CALIFORNIA REDWOOD REGION	INLAND REGION <sup>1</sup>	U.S. SOFTWOOD PLYWOOD PRODUCTION <sup>2</sup>
----- Million board feet -----					Million sq ft, 3/8-inch basis
1970	19,076	7,475	2,374	9,227	14,277
1971	20,631	8,283	2,329	10,019	16,635
1972	21,830	8,983	2,452	10,395	18,324
1973	22,267	9,074	2,629	10,564	18,305
1974	19,425	7,777	2,675	8,973	15,878
1975	17,778	7,139	2,194	8,445	16,050
1976	20,611	8,322	2,500	9,789	18,440
1977	21,558	8,796	2,453	10,309	19,677
1978	20,780	8,845	1,902	10,033	19,936
1979	20,045	8,427	1,838	9,780	20,022
1980	16,429	7,165	1,631	7,633	16,573
1981--					
January	1,402	614	129	659	1,501
February	1,353	590	132	631	1,491
March	1,520	655	125	740	1,618
Total, 1st quarter	4,275	1,859	386	2,030	4,610
April					
May					
June					
Total, 2d quarter					
July					
August					
September					
Total, 3d quarter					
October					
November					
December					
Total, 4th quarter					
1981 total					
----- 1st quarter 1981 change, in percent -----					
From--					
4th quarter 1980	4.6	8.3	-4.0	3.2	3.5
1st quarter 1980	-3.9	-9.0	-10.0	2.8	4.8

Source--Western Wood Products Association, Portland, Oregon (western Washington and western Oregon, inland region), National Forest Products Association, Washington, D.C. (California redwood region), and American Plywood Association, Tacoma, Washington (U.S. softwood plywood data).

<sup>1</sup>Inland region includes eastern Washington, eastern Oregon, California (except redwood region), Nevada, Idaho, Montana, Wyoming, Utah, Colorado, Arizona, New Mexico, and a portion of South Dakota.

<sup>2</sup>Data for 1974 and 1975 are based in part on sampling.



YEAR	TOTAL	OREGON	WASHINGTON	CALIFORNIA	IDAHO, AND COLORADO	SOUTHERN STATES <sup>1</sup>	NORTHERN STATES <sup>2</sup>
1970	14,291.0R	7,439.1	1,804.9	826.8	891.2	3,315.0	14.0
1971	16,642.1R	8,147.9	2,070.0	984.3	1,022.8	4,410.1	7.0
1972	18,323.7	8,634.9	2,251.1	1,050.7	1,068.2	5,318.8	0
1973	18,304.6	8,518.6	2,232.5	963.8	1,031.0	5,558.7	0
1974	15,878.3	7,055.6	1,853.3	843.6	995.7	5,130.1	0
1975	16,050.3	6,927.4	1,723.7	649.6	1,074.1	5,675.5	0
1976	18,440.0	7,917.0	1,894.0	603.0	1,212.0	6,814.0	0
1977	19,376.2	8,109.2	2,013.0	552.0	1,255.0	7,447.0	0
1978	19,964.4	8,226.4	2,084.2	510.7	1,245.0	7,898.1	0
1979	19,653.0	7,929.0	1,727.0	463.0	1,205.0	8,329.0	0
1980	16,468.0	6,179.0	1,333.0	319.0	1,088.0	7,393.0	156.0

Source--American Plywood Association.

<sup>1</sup> Southern States include Alabama, Arkansas, Florida, Georgia, Louisiana, Maryland, North Carolina, Oklahoma, South Carolina, Texas, and Virginia.

<sup>2</sup> Northern States include Maine, Michigan, Minnesota, Wisconsin.

R = revised.

YEAR	DIMENSION, 25 PCT. STD. AND BTR., 2 BY 4 RL, GREEN, S4S, F.O.B. MILL	PONDEROSA PINE BOARDS, NO. 3, 1 BY 12 RL, DRY, S4S, F.O.B. MILL	PONDEROSA PINE NO. 2 SHOP, 6/4 RWRL, S2S, DRY, F.O.B. MILL	DIMENSION STD. AND BTR., 2-IN RWRL, DRY, S4S, F.O.B. MILL	DIMENSION STD. AND BTR., 2-IN RWRL, DRY, S4S, F.O.B. MILL
1970	74.13	84.62	119.82	89.34	77.77
1971	97.77	96.44	152.26	112.38	101.96
1972	117.48	130.94	179.94	141.20	128.93
1973	152.23	179.29	225.65	175.47	167.87
1974	135.05	167.47	244.94	155.28	147.05
1975	137.64	143.28	196.89	149.29	137.55
1976	167.98	184.31	314.44	184.37	175.56
1977	204.76	231.53	377.24	224.34	206.70
1978	227.22	<u>1</u> /258.44	460.00	248.32	237.30
1979	251.34	317.26	478.27	283.06	268.10
1980	197.72	287.52	460.02	223.08	211.23
1981--					
January	NA	NA	NA	NA	NA
February	NA	NA	NA	NA	NA
March	NA	NA	NA	NA	NA
Average, 1st quarter	NA	NA	NA	NA	NA
April					
May					
June					
Average, 2d quarter					
July					
August					
September					
Average, 3d quarter					
October					
November					
December					
Average, 4th quarter					
1981 average					
----- 1st quarter 1981 change, in percent-----					
From--					
4th quarter 1980	NA	NA	NA	NA	NA
1st quarter 1980	NA	NA	NA	NA	NA

Source-U.S. Bureau of Labor Statistics.

111-month average.

NA = not available.

INTERIOR, 1/4-INCH, AD, F.O.B. MILL      EXTERIOR, 3/8-INCH, AC, F.O.B. MILL      INTERIOR SHEATHING, 1/2-INCH, STD. EXT. GLUE, F.O.B. MILL<sup>1</sup>

YEAR

1970	64.34	93.36	--
1971	72.58	103.79	--
1972	87.79	126.44	118.30
1973	111.61	174.50	138.23
1974	125.79	158.27	128.72
1975	131.84	173.00	135.07
1976	144.97	206.61	155.86
1977	162.48	226.44	195.37
1978	191.92	258.51	214.38
1979	201.66	272.90	<u>2</u> /205.79
1980	190.36	253.36	193.51
January	NA	NA	NA
February	NA	NA	NA
March	NA	NA	NA

Average,  
1st quarter

NA      NA      NA

April  
May  
June

Average,  
2d quarter

July  
August  
September

Average,  
3d quarter

October  
November  
December

Average,  
4th quarter

[ 1981 average

- - - - - 1st quarter 1981 change, in percent - - - - -

From--

4th quarter 1980  
1st quarter 1980

NA      NA      NA  
NA      NA      NA

Source--U.S. Bureau of Labor Statistics.

<sup>1</sup>Established January 1972.

<sup>2</sup>11-month average.

NA = not available.

YEAR	TOTAL	PRODUCTS	PRODUCTS	TOTAL	PRODUCTS	PRODUCTS	TOTAL	PRODUCTS	PRODUCTS	TOTAL	PRODUCTS	PRODUCTS
1970	138.2	109.0	29.2	62.0	42.2	19.8	76.2	66.8	9.4	--	2.8	1/
1971	141.2	113.8	27.4	61.5	43.4	18.1	79.7	70.4	9.3	--	2.8	1/
1972	150.2	122.5	27.7	65.5	47.3	18.2	84.7	75.2	9.5	--	2.8	1/
1973	155.3	127.9	27.4	66.8	49.1	17.7	88.5	78.8	9.7	--	2.3	2/
1974	152.1	124.5	27.6	67.3	49.7	17.6	84.8	74.8	10.0	--	2.5	2/
1975	137.2	110.8	26.4	60.4	43.8	16.6	76.8	67.0	9.8	--	2.0	2/
1976	150.9	123.4	27.5	68.4	51.0	17.4	82.5	72.4	10.1	3.4	2.3	1.1
1977	159.2	131.4	27.8	71.6	53.9	17.7	87.6	77.5	10.1	3.6	2.2	1.4
1978	159.3	136.5	22.8	69.1	55.1	14.0	90.2	81.4	8.8	2.9	1.8	1.1
1979	159.0	133.4	25.6	68.4	52.6	15.8	90.6	80.8	9.8	3.0	2.0	1.0
1980	141.2	113.4	27.8	62.5	45.0	17.5	78.7	68.4	10.3	3.4	2.4	1.0
1981--												
January	136.9	109.4	27.5	61.7	44.4	17.3	75.2	65.0	10.2	2.1	1.2	.9
February	136.6	109.3	27.3	61.9	44.7	17.2	74.7	64.6	10.1	2.3	1.4	.9
March	135.4	108.4	27.0	61.2	44.4	16.8	74.2	64.0	10.2	2.8	1.9	.9
Average, 1st quarter	136.3	109.0	27.3	61.6	44.5	17.1	74.7	64.5	10.2	2.4	1.5	.9
April												
May												
June												
Average, 2d quarter												
July												
August												
September												
Average, 3d quarter												
October												
November												
December												
Average, 4th quarter												
1981 average												
----- 1st quarter 1981 change in employment -----												
From--												
4th quarter												
1980	-3.2R	-2.1	-1.1R	-.8R	.2R	-1.0R	-2.4	-2.3	-.1	-.4	-.4	0
1st quarter												
1980	-14.6R	-13.7	-.9R	-4.6R	-3.9R	-.7R	10.0R	-9.8R	-.2	.5	.1	.4

Source—State employment agencies. Includes both covered and noncovered employment. The lumber and wood products industry includes logging, lumber, plywood, poles and piling, and miscellaneous wood products (excludes furniture). The paper and allied products industry includes pulp, paper, paperboard, and building board products. Since April 1974, employment data have been based on place of residence.

<sup>1</sup>Before 1973, data for the pulp and allied products industry are included in the lumber and wood products industry.

<sup>2</sup>Withheld to avoid disclosure.

R = revised.

YEAR	TOTAL	LUMBER AND WOOD PRODUCTS	PAPER AND ALLIED PRODUCTS
1970	84.8	48.1	36.7
1971	86.0	50.5	35.5
1972	90.3	52.4	37.9
1973	90.2	54.1	36.1
1974	88.2	50.9	37.3
1975	87.3	52.8	34.5
1976	96.6	59.9	36.7
1977	104.2	66.6	37.6
1978	107.1	69.9	37.2
1979	107.8	68.7	39.1
1980--			
January	101.9	62.5	39.4
February	101.8	62.4	39.4
March	102.1	62.4	39.7
Average, 1st quarter	101.9	62.4	39.5
April	100.5	61.1	39.4
May	98.7	59.8	38.9
June	100.4	61.9	38.5
Average, 2d quarter	99.8	60.9	38.9
July	102.0	63.6	38.4
August	102.1	63.8	38.3
September	103.1	64.6	38.5
Average, 3d quarter	102.4	64.0	38.4
October	102.7	64.6	38.1
November	101.2	63.3	37.9
December	98.8	60.9	37.9
Average, 4th quarter	100.9	62.9	38.0
1980 average	101.3	62.6	38.7
- - - 4th quarter 1980 change in employment - - -			
From--			
3d quarter 1980	-1.5	-1.1	-.4
4th quarter 1979	-6.4	-5.1	-1.3
- - - Year 1980 change in employment - - -			
From year 1979	-6.5	-6.1	-.4

Source--State of California, Department of Employment. Since April 1974, data have been based on place of residence.



YEAR	LUMBER AND WOOD PRODUCTS	PAPER AND ALLIED PRODUCTS	TOTAL	LUMBER AND WOOD PRODUCTS	PAPER AND ALLIED PRODUCTS
1970	8.2	1/	13.8	12.8	1.0
1971	8.7	1/	14.8	13.7	1.1
1972	9.2	1/	15.2	14.1	1.1
1973	9.8	1/	16.3	15.1	1.2
1974	9.5	1/	15.7	14.6	1.1
1975	8.1	1/	16.8	15.7	1.1
1976	9.1	1/	18.6	17.4	1.2
1977	9.3	1/	19.0	17.8	1.2
1978	10.7	1/	20.1	18.8	1.3
1979	11.0	1/	19.9	18.5	1.4
1980	8.8	1/	17.5	16.1	1.4
1981					
January	9.1	1/	17.2	15.7	1.5
February	8.9	1/	17.2	15.7	1.5
March	8.8	1/	16.1	14.6	1.5
Average, 1st quarter	8.9	1/	16.8	15.3	1.5
April					
May					
June					
Average, 2d quarter					
July					
August					
September					
Average, 3d quarter					
October					
November					
December					
Average, 4th quarter					
1981 average					
- - - - - 1st quarter 1981 change in employment - - - - -					
From--					
4th quarter 1980	.4	--	-1.3	-1.3	0.
1st quarter 1980	-.8R	--	-.6R	-.7R	.1R

Source--State employment agencies. Since April 1974, employment data have been based on place of residence.

1/Withheld to avoid disclosing figures for individual companies.

R = revised.

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
TO ALL COUNTRIES											
1970	2,216,110	452,655	41,260	1,722,195	1,579,185	308,466	1,270,719	636,925	144,189	41,260	451,476
1971	1,837,173	416,453	34,390	1,386,330	1,319,809	294,430	1,025,379	517,364	122,023	34,390	360,951
1972	2,637,148	767,496	36,907	1,832,745	1,907,235	566,487	1,340,748	729,913	201,009	36,907	491,997
1973	2,639,210	864,474	20,966	1,753,770	1,833,293	555,324	1,277,969	805,917	309,150	20,966	475,801
1974	2,189,367	715,514	17,481	1,456,372	1,423,570	404,884	1,018,686	765,797	310,630	17,481	437,686
1975	2,225,487	765,840	24,361	1,435,286	1,427,387	437,290	990,097	798,100	328,550	24,361	445,189
1976	2,737,074	945,649	26,576	1,764,849	1,792,944	527,889	1,265,055	944,130	417,760	26,576	499,794
1977	2,555,615	966,763	16,721	1,572,131	1,674,860	556,419	1,118,441	880,755	410,344	16,721	453,690
1978	2,847,394	1,139,267	24,493	1,683,634	1,915,979	619,500	1,296,479	931,415	519,767	24,493	387,155
1979	3,233,652	1,309,179	22,693	1,901,780	2,249,963	732,392	1,517,571	983,689	576,787	22,693	384,209
1980--											
1st qtr.	827,738	369,910	3,440	454,388	547,829	193,213	354,616	279,909	176,697	3,440	99,772
2d qtr.	793,840	358,563	4,704	430,573	539,841	189,551	350,290	253,999	169,012	4,704	80,283
3d qtr.	508,640	265,986	2,249	240,405	309,541	132,270	177,271	199,099	133,716	2,249	63,134
4th qtr.	501,599	267,751	1,907	231,941	301,927	130,039	171,888	199,672	137,712	1,907	60,053
1980 total	2,631,817	1,262,210	12,300	1,357,307	1,699,138	645,073	1,054,065	932,679	617,137	12,300	303,242
1981--											
1st qtr.	519,222	251,035	5,505	262,682	333,359	128,237	205,122	185,863	122,798	5,505	57,560
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											
JAPAN											
1970	2,144,332	430,634	41,254	1,672,444	1,514,695	290,158	1,224,537	629,637	140,476	41,254	447,907
1971	1,710,299	390,978	34,390	1,284,931	1,197,011	271,763	925,248	513,288	119,215	34,390	359,683
1972	2,391,163	692,308	36,907	1,661,948	1,678,846	496,201	1,182,645	712,317	196,107	36,907	479,303
1973	2,455,485	822,160	20,966	1,612,359	1,663,203	520,373	1,142,830	792,282	301,787	20,966	469,529
1974	1,975,575	638,225	17,342	1,320,008	1,237,653	341,890	895,763	737,922	296,335	17,342	424,245
1975	2,014,244	732,264	24,361	1,257,619	1,255,817	410,721	845,096	758,427	321,543	24,361	412,523
1976	2,547,037	901,911	24,573	1,620,553	1,623,064	491,451	1,131,613	923,973	410,460	24,573	488,940
1977	2,348,325	933,813	16,721	1,397,791	1,496,627	526,255	970,372	851,698	407,558	16,721	427,419
1978	2,521,885	1,103,562	22,814	1,395,509	1,630,247	509,654	1,040,593	891,638	513,908	22,814	354,916
1979	2,959,726	1,279,177	20,611	1,659,938	1,998,315	705,921	1,292,394	961,411	573,256	20,611	367,544
1980--											
1st qtr.	758,470	363,052	3,440	391,978	491,160	189,294	301,866	267,310	173,758	3,440	90,112
2d qtr.	727,929	352,551	4,704	370,674	481,535	185,236	296,299	246,394	167,315	4,704	74,375
3d qtr.	460,916	250,857	2,249	207,810	270,364	120,840	149,524	190,552	130,017	2,249	58,286
4th qtr.	397,007	208,947	1,907	186,153	245,435	107,235	138,200	151,572	101,712	1,907	47,953
1980 total	2,344,322	1,175,407	12,300	1,156,615	1,488,494	602,605	885,889	855,828	572,802	12,300	270,726
1981--											
1st qtr.	423,412	221,734	5,505	196,173	252,904	107,354	145,550	170,508	114,380	5,505	50,623
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
TO CANADA											
1970	27,997	11,171	--	16,826	27,997	11,171	16,826	--	--	--	--
1971	55,712	12,332	--	43,380	55,712	12,332	43,380	--	--	--	--
1972	170,582	43,294	--	127,288	159,359	43,294	116,065	11,223	--	--	11,223
1973	72,164	22,265	--	49,899	72,164	22,265	49,899	--	--	--	--
1974	73,664	39,060	--	34,604	73,664	39,060	34,604	--	--	--	--
1975	58,506	16,793	--	41,713	58,506	16,793	41,713	--	--	--	--
1976	48,289	14,803	--	33,486	48,289	14,803	33,486	--	--	--	--
1977	15,698	9,531	--	6,167	15,698	9,531	6,167	--	--	--	--
1978	12,638	9,361	--	3,277	12,638	9,361	3,277	--	--	--	--
1979	24,124	7,737	--	16,387	24,124	7,737	16,387	--	--	--	--
1980--											
1st qtr.	153	77	--	76	153	77	76	--	--	--	--
2d qtr.	247	49	--	98	247	49	198	--	--	--	--
3d qtr.	264	61	--	203	264	61	203	--	--	--	--
4th qtr.	321	208	--	113	321	208	113	--	--	--	--
1980 total	985	395	--	590	985	395	590	--	--	--	--
1981											
1st qtr.	634	239	--	395	634	239	395	--	--	--	--
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											
TO SOUTH KOREA											
1970	32,336	5,140	--	27,196	26,839	3,138	23,701	5,497	2,002	--	3,495
1971	63,757	6,331	--	57,426	62,757	6,331	56,426	1,000	--	--	1,000
1972	47,554	4,419	--	43,135	46,304	4,419	41,885	1,250	--	--	1,250
1973	101,929	15,175	--	86,754	96,680	12,063	84,617	5,249	3,112	--	2,137
1974	137,665	36,308	--	101,357	111,580	23,378	88,202	26,085	12,930	--	13,155
1975	79,022	13,946	--	65,076	42,100	9,100	33,000	36,922	4,846	--	32,076
1976	130,069	26,454	--	103,615	117,007	21,068	95,939	13,062	5,386	--	7,676
1977	187,967	21,201	--	166,766	162,252	20,418	141,834	25,715	783	--	24,932
1978	307,865	24,844	--	283,021	271,887	20,426	251,461	35,978	4,418	--	31,560
1979	245,314	20,342	--	224,972	227,072	18,653	208,419	18,242	1,689	--	16,553
1980--											
1st qtr.	67,479	5,386	--	62,093	56,375	3,782	52,593	11,104	1,604	--	9,500
2d qtr.	59,802	1,094	--	58,708	53,477	677	52,800	6,325	417	--	5,908
3d qtr.	32,084	1,861	--	30,223	27,547	1,861	25,686	4,537	--	--	4,537
4th qtr.	32,022	3,455	--	28,567	26,589	3,229	23,360	5,433	226	--	5,207
1980 total	191,387	11,796	--	179,591	163,988	9,549	154,439	27,399	2,247	--	25,152
1981--											
1st qtr.	47,994	3,781	--	44,213	47,097	3,279	43,818	897	502	--	395
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											
TO MAINLAND CHINA											
1980--											
1st qtr.	--	--	--	--	--	--	--	--	--	--	--
2d qtr.	3,584	3,584	--	--	3,584	3,584	--	--	--	--	--
3d qtr.	14,357	13,101	--	1,256	10,733	9,508	1,225	3,624	3,593	--	31
4th qtr.	69,844	53,216	--	16,628	28,954	18,792	10,162	40,890	34,424	--	6,466
1980 total	87,785	69,901	--	17,884	43,271	31,884	11,387	44,514	38,017	--	6,497
1981--											
1st qtr.	43,381	23,684	--	19,697	31,378	16,159	15,219	12,003	7,525	--	4,478
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											

Source--U.S. Department of Commerce. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
TO ALL COUNTRIES											
1970	280,920	54,109	13,611	213,200	193,476	37,015	156,461	87,444	17,094	13,611	56,739
1971	233,304	49,773	10,926	172,605	162,343	35,141	127,202	70,961	14,632	10,926	45,403
1972	358,713	101,467	12,089	245,157	252,839	73,175	179,664	105,874	28,292	12,089	65,493
1973	694,602	209,417	15,451	469,734	449,902	120,796	329,106	244,700	88,621	15,451	140,628
1974	612,521	194,137	17,556	400,828	364,962	103,586	271,376	237,559	90,551	17,556	129,452
1975	603,854	202,377	16,758	384,759	376,706	111,919	264,787	227,148	90,418	16,758	119,972
1976	775,113	266,523	20,086	488,504	490,246	141,989	348,257	284,867	124,534	20,087	140,247
1977	826,698	311,269	17,049	498,380	526,412	171,541	354,871	300,286	139,728	17,049	143,509
1978	992,207	413,645	24,923	553,639	637,818	212,305	425,513	354,389	201,340	24,923	128,126
1979	1,408,036	624,090	24,419	831,527	991,513	331,874	659,639	488,523	292,216	24,419	171,188
1980--											
1st qtr.	425,175	192,752	5,368	227,055	276,019	97,683	178,336	149,156	95,069	5,368	48,719
2d qtr.	407,304	186,597	5,857	214,850	273,041	96,761	176,280	134,263	89,836	5,857	38,570
3d qtr.	246,182	130,256	2,800	113,126	149,637	63,905	85,732	96,545	66,351	2,800	27,394
4th qtr.	230,197	125,293	2,571	102,333	136,827	59,395	77,432	93,370	65,898	2,571	24,901
1980 total	1,308,858	634,898	16,596	657,364	835,524	317,744	517,780	473,334	317,154	16,596	139,584
1981--											
1st qtr.	233,027	118,446	8,158	106,423	144,701	60,167	84,534	88,326	58,279	8,158	21,889
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											
TO JAPAN											
1970	273,988	52,051	13,608	208,329	187,237	35,294	151,943	86,751	16,757	13,608	56,386
1971	219,543	46,966	10,926	161,651	149,120	32,756	116,364	70,423	14,210	10,926	45,287
1972	335,703	94,210	12,089	229,404	231,593	66,800	164,793	104,110	27,410	12,089	64,611
1973	664,363	201,944	15,451	446,968	422,715	115,022	307,693	241,648	86,922	15,451	139,275
1974	569,494	177,961	17,500	374,033	338,296	90,400	247,896	231,198	87,561	17,500	126,137
1975	560,754	195,469	16,758	348,527	341,885	107,149	234,736	218,869	88,320	16,758	113,791
1976	734,412	256,673	17,918	459,821	457,248	134,894	322,354	277,164	121,779	17,918	137,467
1977	776,630	303,248	17,049	456,333	484,006	164,626	319,380	292,624	138,622	17,049	136,953
1978	908,627	404,134	22,763	481,730	566,494	204,832	361,662	342,133	199,302	22,763	120,068
1979	1,387,602	612,160	22,271	753,171	910,338	323,034	587,304	477,264	289,126	22,271	165,867
1980--											
1st qtr.	398,458	189,888	5,368	203,202	254,399	96,324	158,075	144,059	93,564	5,368	45,127
2d qtr.	379,364	182,562	5,857	190,945	248,492	94,003	154,489	130,872	88,559	5,857	36,456
3d qtr.	225,699	122,119	2,800	100,780	132,636	57,754	74,882	93,063	64,365	2,800	25,898
4th qtr.	187,354	98,915	2,571	85,868	114,842	49,278	65,564	72,512	49,637	2,571	20,304
1980 total	1,190,875	593,484	16,596	580,795	750,369	297,359	453,010	440,506	296,125	16,596	127,785
1981--											
1st qtr.	197,679	106,012	8,158	83,509	115,580	51,466	64,114	82,099	54,546	8,158	19,395
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	TOTAL	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
TO CANADA											
1970	2,023	863	--	1,160	2,023	863	1,160	--	--	--	--
1971	4,892	1,240	--	3,652	4,892	1,240	3,652	--	--	--	--
1972	14,041	2,984	--	11,057	13,349	2,984	10,365	692	--	--	692
1973	9,593	2,900	--	6,693	9,593	2,900	6,693	--	--	--	--
1974	13,821	8,239	--	5,582	13,821	8,239	5,582	--	--	--	--
1975	8,313	2,937	--	5,376	8,313	2,937	5,376	--	--	--	--
1976	7,908	2,733	--	5,175	7,908	2,733	5,175	--	--	--	--
1977	3,545	2,154	--	1,391	3,545	2,154	1,391	--	--	--	--
1978	2,933	2,129	--	804	2,933	2,129	804	--	--	--	--
1979	7,223	2,435	--	4,788	7,223	2,435	4,788	--	--	--	--
1980--											
1st qtr.	44	22	--	22	44	22	22	--	--	--	--
2d qtr.	77	23	--	54	77	23	54	--	--	--	--
3d qtr.	88	20	--	68	88	20	68	--	--	--	--
4th qtr.	114	68	--	46	114	68	46	--	--	--	--
1980 total	323	133	--	190	323	133	190	--	--	--	--
1981--											
1st qtr.	253	107	--	146	253	107	146	--	--	--	--
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											
TO SOUTH KOREA											
1970	3,659	559	--	3,100	3,174	416	2,758	485	143	--	342
1971	7,950	728	--	7,222	7,863	728	7,135	87	--	--	87
1972	5,094	469	--	4,625	4,939	469	4,470	155	--	--	155
1973	18,506	3,468	--	15,038	17,290	2,725	14,565	1,216	743	--	473
1974	28,225	7,303	--	20,922	22,552	4,714	17,838	5,673	2,589	--	3,084
1975	14,757	2,688	--	12,069	7,912	1,648	6,264	6,845	1,040	--	5,805
1976	27,546	5,664	--	21,882	24,400	4,350	20,050	3,146	1,315	--	1,831
1977	44,949	4,811	--	40,138	38,738	4,672	34,066	6,211	139	--	6,072
1978	76,839	6,392	--	70,447	67,974	5,333	62,641	8,865	1,059	--	7,806
1979	80,173	6,982	--	73,191	73,751	6,378	67,373	6,422	604	--	5,818
1980--											
1st qtr.	25,471	1,903	--	23,568	21,448	1,306	20,142	4,023	597	--	3,426
2d qtr.	23,687	330	--	23,357	21,421	178	21,243	2,266	152	--	2,114
3d qtr.	11,590	617	--	10,973	10,237	617	9,620	1,353	--	--	1,353
4th qtr.	10,927	1,266	--	9,661	9,002	1,178	7,824	1,925	88	--	1,837
1980 total	71,675	4,116	--	67,559	62,108	3,279	58,829	9,567	837	--	8,730
1981--											
1st qtr.	16,024	1,276	--	14,748	15,720	1,108	14,612	304	168	--	136
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											
TO MAINLAND CHINA											
1980--											
1st qtr.	--	--	--	--	--	--	--	--	--	--	--
2d qtr.	2,553	2,553	--	--	2,553	2,553	--	--	--	--	--
3d qtr.	8,153	7,456	--	697	6,202	5,514	688	1,951	1,942	--	9
4th qtr.	30,727	24,276	--	6,451	12,571	8,625	3,946	18,156	15,651	--	2,505
1980 total	41,433	34,285	--	7,148	21,326	16,692	4,634	20,107	17,593	--	2,514
1981--											
1st qtr.	17,796	1,040	--	7,392	12,594	6,991	5,603	5,202	3,413	--	1,789
2d qtr.											
3d qtr.											
4th qtr.											
1981 total											

Source--U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

YEAR AND QUARTER	ALL SPECIES	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	ALL SPECIES	DOUGLAS- FIR	OTHER SOFTWOODS	ALL SPECIES	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
TO ALL COUNTRIES											
1970	126.76	119.54	329.88	123.80	122.52	120.00	123.13	137.29	118.55	329.88	125.67
1971	126.99	119.52	317.70	124.51	123.00	119.35	124.05	137.16	119.91	317.70	125.79
1972	136.02	132.21	327.56	133.76	132.57	129.17	134.00	145.05	140.75	327.56	133.12
1973	263.19	242.25	736.97	267.84	245.41	217.52	257.52	303.63	286.66	736.97	295.56
1974	279.77	271.33	1,004.29	275.22	263.40	255.84	266.40	310.21	291.51	1,004.29	295.76
1975	271.34	264.20	687.90	268.07	263.91	255.94	267.43	284.61	275.20	687.90	269.49
1976	283.19	281.84	755.83	276.80	273.43	268.98	275.29	301.73	298.10	755.83	280.61
1977	323.48	321.97	1,019.62	317.01	314.30	308.29	317.26	340.94	340.51	1,019.62	316.32
1978	348.46	363.08	1,017.56	328.84	332.89	342.70	328.21	380.48	387.37	1,017.56	330.94
1979	435.43	476.70	1,076.06	437.24	440.68	453.14	434.67	496.62	506.62	1,076.06	445.56
1980--											
1st qtr.	513.66	521.08	1,560.44	499.69	503.84	505.57	502.90	532.87	538.04	1,560.44	488.30
2d qtr.	513.08	520.40	1,245.03	498.99	505.78	510.48	503.24	528.60	531.54	1,245.03	480.43
3d qtr.	484.00	489.71	1,245.05	470.56	483.41	483.14	483.62	484.91	496.21	1,245.05	433.90
4th qtr.	458.93	467.95	1,348.42	441.20	453.18	456.75	450.48	467.62	478.52	1,348.42	414.65
1980 average	497.32	503.00	1,349.27	484.32	491.73	492.57	491.22	507.50	513.91	1,349.27	460.31
1981--											
1st qtr.	448.80	471.83	1,481.97	405.14	434.07	469.18	412.11	475.22	474.59	1,481.97	380.28
2d qtr.											
3d qtr.											
4th qtr.											
1981 average											
TO JAPAN											
1970	127.77	120.87	329.86	124.57	123.61	121.64	124.08	137.78	119.29	329.86	125.89
1971	128.36	120.12	317.70	125.81	124.58	120.53	125.77	137.20	119.19	317.70	125.91
1972	140.39	136.08	327.56	138.03	137.95	134.62	139.34	146.16	139.77	327.56	134.80
1973	270.56	245.63	736.97	277.21	254.16	221.04	269.24	305.00	288.03	736.97	296.63
1974	288.27	278.84	1,009.12	283.36	273.34	264.41	276.74	313.31	295.48	1,009.12	297.32
1975	278.39	266.94	687.90	277.13	272.24	260.88	277.76	288.58	274.68	687.90	275.84
1976	288.34	284.59	729.17	283.74	281.72	274.48	284.86	299.97	296.69	729.17	281.15
1977	330.72	324.74	1,019.62	326.47	323.40	312.83	329.13	343.58	340.13	1,019.62	320.42
1978	360.30	366.21	997.76	345.20	347.49	347.38	347.55	383.71	387.82	997.76	338.30
1979	468.83	478.56	1,080.54	453.73	455.55	457.61	454.43	496.42	504.36	1,080.54	451.28
1980--											
1st qtr.	525.34	523.03	1,560.44	518.40	517.96	508.86	523.66	538.92	538.47	1,560.44	500.79
2d qtr.	521.16	517.83	1,245.03	515.13R	516.04R	507.48	521.39	531.15	529.30	1,245.03	490.17
3d qtr.	489.67	486.80	1,245.05	484.96	490.58	477.93	500.80	488.39	495.05	1,245.05	444.33
4th qtr.	471.92	473.40	1,348.42	461.28	467.91	459.53	474.42	478.40	488.02	1,348.42	423.41
1980 average	507.98	504.92	1,349.27	502.15	504.11	493.35	511.36	514.71	516.98	1,349.27	472.01
1981--											
1st qtr.	466.87	478.10	1,481.97	425.69	457.01	479.40	440.49	481.50	476.89	1,481.97	383.13
2d qtr.											
3d qtr.											
4th qtr.											
1981 average											



YEAR AND QUARTER	ALL SPECIES	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS	ALL SPECIES	DOUGLAS- FIR	OTHER SOFTWOODS	ALL SPECIES	DOUGLAS- FIR	PORT ORFORD- CEDAR	OTHER SOFTWOODS
TO CANADA											
1970	72.26	77.23	--	68.96	72.26	77.23	68.96	--	--	--	--
1971	87.80	100.55	--	84.18	87.80	100.55	84.18	--	--	--	--
1972	82.31	68.93	--	86.86	83.77	68.93	80.30	61.66	--	--	61.66
1973	132.94	130.26	--	134.14	132.94	130.26	134.14	--	--	--	--
1974	187.62	210.93	--	161.31	187.62	210.93	161.31	--	--	--	--
1975	142.09	174.89	--	128.88	142.09	174.89	128.88	--	--	--	--
1976	163.76	184.62	--	154.54	163.76	184.62	154.54	--	--	--	--
1977	225.82	226.00	--	225.56	225.82	226.00	225.56	--	--	--	--
1978	232.08	227.43	--	245.35	232.08	227.43	245.35	--	--	--	--
1979	299.41	314.72	--	292.78	299.41	314.72	292.18	--	--	--	--
1980--											
1st qtr.	289.39	290.00	--	288.78	289.39	290.00	288.78	--	--	--	--
2d qtr.	313.79	476.61	--	273.49	319.79	476.61	273.49	--	--	--	--
3d qtr.	334.95	333.44	--	335.40	334.95	333.44	335.40	--	--	--	--
4th qtr.	356.11	329.61	--	404.89	356.11	329.61	404.89	--	--	--	--
1980 average	327.92	336.71	--	322.03	327.92	336.71	322.03	--	--	--	--
1981--											
1st qtr.	398.65	446.78	--	369.52	398.65	446.78	369.52	--	--	--	--
2d qtr.											
3d qtr.											
4th qtr.											
1981 average											
TO SOUTH KOREA											
1970	113.14	108.63	--	113.99	118.27	132.53	116.38	88.08	71.18	--	97.77
1971	124.70	115.00	--	125.77	125.30	115.00	126.46	87.00	--	--	87.00
1972	107.12	106.10	--	107.22	106.66	106.10	106.72	124.00	--	--	124.00
1973	181.54	228.47	--	173.34	178.83	225.89	172.12	231.52	238.47	--	221.40
1974	205.03	201.12	--	206.43	202.12	201.62	202.26	217.47	200.23	--	234.41
1975	186.74	192.74	--	185.46	187.93	181.10	189.82	185.39	214.61	--	180.98
1976	211.78	214.11	--	211.19	208.53	206.47	208.93	240.77	244.77	--	238.54
1977	239.13	226.92	--	240.68	238.75	228.82	240.18	241.53	177.52	--	243.54
1978	249.59	257.28	--	249.02	250.01	261.09	249.11	246.40	239.70	--	247.34
1979	326.82	343.23	--	325.33	324.79	341.93	323.26	352.05	357.61	--	351.48
1980--											
1st qtr.	377.47	353.28	--	379.57	380.46	345.26	382.99	362.32	372.19	--	360.66
2d qtr.	396.10	302.01	--	397.86	400.57	263.22	402.33	358.31	365.00	--	357.84
3d qtr.	361.23	331.55	--	363.06	371.61	331.55	374.51	298.22	--	--	298.22
4th qtr.	341.23	366.48	--	338.18	338.57	364.77	334.94	354.27	390.86	--	352.69
1980 average	374.50	348.93	--	376.18	378.74	343.39	380.92	349.17	372.50	--	347.09
1981--											
1st qtr.	333.88	337.43	--	333.57	333.70	337.80	333.48	339.09	334.98	--	344.30
2d qtr.											
3d qtr.											
4th qtr.											
1981 average											
TO MAINLAND CHINA											
1980--											
1st qtr.	--	--	--	--	--	--	--	--	--	--	--
2d qtr.	712.46	712.46	--	--	712.46	712.46	--	--	--	--	--
3d qtr.	567.93	569.15	--	555.29	577.87	579.94	561.79	538.53	540.60	--	298.45
4th qtr.	439.95	456.18	--	388.00	434.19	458.97	388.35	444.02	454.65	--	387.44
1980 average	471.98	490.48	--	399.69	492.85	523.52	406.96	451.70	462.77	--	386.95
1981--											
1st qtr.	410.23	439.28	--	375.30	401.37	432.62	368.19	433.40	453.59	--	399.46
2d qtr.											
3d qtr.											
4th qtr.											
1981 average											

Source--U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

YEAR AND QUARTER	TOTAL	DOUGLAS-FIR	PORT-ORFORD- CEDAR	OTHER SOFTWOODS
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TO ALL COUNTRIES

1970	192,083	32,531	2,894	156,658
1971	102,408	27,032	2,182	73,194
1972	77,459	18,337	3,418	55,704
1973	104,733	34,454	4,065	66,214
1974	77,735	35,146	8,823	33,766
1975	86,943	52,547	2,483	31,913
1976	109,812	73,924	2,508	33,380
1977	70,902	38,302	2,331	30,269
1978	72,650	49,024	2,880	20,746
1979	65,492	37,551	1,611	26,330
1980—				
1st quarter	6,517	3,174	--	3,343
2d quarter	2,506	--	--	2,506
3d quarter	13,230	2,492	--	10,738
4th quarter	9,419	1,621	653	7,145

1980 total	31,672	7,287	653	23,732
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1981—				
1st quarter	10,123	1,026	360	8,737
2d quarter				
3d quarter				
4th quarter				

1981 total

TO JAPAN

1970	175,217	29,965	2,894	142,358
1971	93,281	26,712	2,182	64,387
1972	68,830	15,914	3,418	49,498
1973	94,520	29,261	4,065	61,194
1974	69,271	32,485	8,823	27,963
1975	78,813	48,188	2,483	28,142
1976	96,485	69,395	2,853	24,237
1977	57,815	37,765	2,331	17,719
1978	58,760	48,653	1,757	8,350
1979	57,938	37,411	1,611	18,916
1980—				
1st quarter	6,517	3,174	--	3,343
2d quarter	402	--	--	402
3d quarter	13,194	2,492	--	10,702
4th quarter	7,067	1,389	653	5,025

1980 total	27,180	7,055	653	19,472
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1981—				
1st quarter	10,105	1,020	360	8,725
2d quarter				
3d quarter				
4th quarter				

1981 total

Source—U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

<sup>1</sup>Northern California consists of the San Francisco Customs District and includes Monterey, California, and all ports north of Monterey.

YEAR AND QUARTER	ABERDEEN	ANACORTES, BELLINGHAM	EVERETT	LONGVIEW	OLYMPIA	PORT ANGELES	TACOMA	NORTHEASTERN WASHINGTON	OTHER	TOTAL
1970	335.6	66.0	274.8	153.3	210.6	242.9	356.4	--	79.5	1,739.1
1971	297.5	104.5	221.4	125.7	120.1	212.9	323.1	--	41.0	1,446.2
1972	525.1	100.9	268.9	221.3	144.6	285.6	517.4	.2	45.8	2,109.8
1973	491.5	84.5	250.4	328.7	86.9	306.0	511.1	0	54.6	2,113.7
1974	396.2	49.2	217.7	300.2	61.5	273.5	383.0	--	48.4	1,729.7
1975	366.8	32.2	230.0	261.3	48.6	284.7	469.2	--	32.9	1,725.7
1976	502.1	30.5	277.2	397.4	7.5	324.5	623.7	0	28.5	2,191.4
1977	402.1	42.1	237.7	328.2	68.7	304.6	607.6	--	12.0	2,003.0
1978	512.2	41.1	321.8	325.8	87.1	387.2	559.7	--	7.0	2,241.0
1979	648.7	50.9	332.8	366.1	101.0	505.0	601.7	--	9.9	2,616.1
1980--										
1st quarter	144.3	9.8	99.7	131.2	27.5	102.2	163.5	0	.8	679.0
2d quarter	159.5	13.3	81.0	96.4	30.3	105.3	150.0	0	.5	636.3
3d quarter	88.7	6.0	52.7	83.7	15.2	50.3	95.6	0	1.0	393.2
4th quarter	105.7	8.9	53.9	75.7	7.2	37.3	88.0	.1	.8	377.6
1980 total	498.2	38.0	287.3	387.0	80.2	295.1	497.1	.1	3.1	2,086.1
1981--										
1st quarter	109.6	7.6	66.1	61.6	14.7	44.5	90.1	.1	.7	395.0
2d quarter										
3d quarter										
4th quarter										
1981 total										

YEAR AND QUARTER	STATE OF OREGON <sup>1</sup>					NORTHERN CALIFORNIA				
	ASTORIA	COOS BAY	PORTLAND	OTHER	TOTAL	EUREKA	REDWOOD CITY	SACRAMENTO	STOCKTON	OTHER
1970	219.1	114.1	143.9	--	477.1	93.6	4.6	73.1	2.9	17.9
1971	194.1	84.2	112.7	--	391.0	65.9	1.2	35.3	--	0
1972	262.6	121.0	115.5	9.4	508.5	51.9	--	2.8	19.4	.9
1973	147.1	155.5	159.8	21.3	483.7	79.6	0	16.2	8.7	.2
1974	159.0	128.1	139.8	24.8	451.7	67.5	0	9.8	3.8	.2
1975	245.7	134.1	137.5	44.5	561.8	66.6	0	19.9	0	1.4
1976	273.3	144.6	99.5	28.0	545.4	83.7	0	26.1	0	--
1977	210.2	120.1	207.0	15.4	552.7	39.2	0	25.5	0	6.3
1978	168.4	145.1	277.0	15.0	605.5	46.1	0	18.4	--	8.2
1979	150.1	128.2	322.0	17.2	617.5	43.0	0	6.0	0	16.5
1980--										
1st quarter	49.9	43.8	55.0	0	148.7	3.3	0	0	.5	2.7
2d quarter	28.9	36.6	92.1	0	157.6	2.3	0	0	0	.2
3d quarter	26.4	25.3	63.7	0	115.4	4.4	0	0	0	8.8
4th quarter	29.5	29.5	65.0	0	124.0	4.9	0	3.9	0	.6
1980 total	134.7	135.2	275.8	0	545.7	14.9	0	3.9	.5	12.3
1981--										
1st quarter	17.1	30.1	77.0	0	124.2	0	0	9.7	0	.4
2d quarter										
3d quarter										
4th quarter										
1981 total										

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

<sup>1</sup>State totals as presented here for Washington and Oregon do not agree with those found in table 8 because customs districts as used in table 8 do not correspond to State boundaries.

YEAR AND QUARTER	ABERDEEN	ANACORTES, BELLINGHAM	EVERETT	LONGVIEW	OLYMPIA	PORT ANGELES	TACOMA	NORTHEASTERN WASHINGTON	OTHER	AVERAGE
1970	123.34	126.47	132.64	121.51	119.33	118.50	118.44	--	120.18	122.46
1971	128.46	124.42	125.73	126.51	127.76	120.37	116.15	--	118.62	123.30
1972	134.28	128.21	129.47	144.82	146.76	129.52	131.82	146.73	123.50	133.86
1973	264.23	211.35	258.69	288.82	284.15	215.32	262.90	0	229.45	257.80
1974	266.16	261.07	257.85	292.13	282.38	246.79	274.24	--	262.10	268.58
1975	256.17	297.84	273.29	280.90	273.90	253.46	266.63	--	279.01	266.30
1976	269.90	293.96	287.08	302.53	302.53	261.25	277.21	0	252.97	277.26
1977	311.97	296.28	309.82	336.01	331.68	294.59	327.76	--	263.80	317.86
1978	332.92	295.77	334.87	379.57	347.93	319.97	340.91	--	344.67	339.68
1979	452.52	376.18	455.44	518.19	499.12	424.46	428.19	--	492.38	451.64
1980--										
1st quarter	486.07	436.80	484.36	534.24	508.39	487.89	544.33	0	570.37	509.72
2d quarter	504.79	415.50	493.89	515.32	528.19	486.42	530.12	0	562.24	507.23
3d quarter	510.11	464.31	465.28	469.80	484.09	467.55	504.75	0	589.61	487.26
4th quarter	458.69	354.40	430.62	488.23	501.15	394.43	491.70	280.95	435.37	460.20
1980 average	490.53	414.44	473.47	506.59	510.63	472.08	523.11	280.95	538.84	495.76
1981--										
1st quarter	408.10	432.05	417.82	469.31	514.43	381.89	490.67	307.74	405.07	439.57
2d quarter										
3d quarter										
4th quarter										
1981 average										

YEAR AND QUARTER	STATE OF OREGON <sup>1</sup>					NORTHERN CALIFORNIA					
	ASTORIA	COOS BAY	PORTLAND	OTHER	AVERAGE	EUREKA	REDWOOD CITY	SACRAMENTO	STOCKTON	OTHER	AVERAGE
1970	121.59	199.84	128.71	--	142.46	111.22	90.00	114.04	96.95	92.28	109.81
1971	117.61	212.89	126.33	--	140.64	107.55	126.58	110.37	--	0	108.76
1972	127.03	194.93	144.27	140.31	147.35	129.24	--	189.29	179.64	129.17	144.52
1973	321.16	348.95	289.64	257.16	316.88	219.99	0	226.77	296.78	363.54	227.72
1974	300.21	363.95	302.18	291.33	318.41	295.56	0	317.05	328.16	252.62	299.55
1975	236.89	349.97	316.25	271.48	286.03	256.07	0	368.11	0	452.10	284.62
1976	267.63	372.46	337.44	253.76	307.45	292.15	0	367.73	0	--	312.31
1977	338.29	409.01	328.22	318.00	349.32	333.34	0	337.06	0	338.45	335.14
1978	325.32	512.44	366.77	330.78	389.23	353.99	0	362.18	--	372.07	358.09
1979	461.34	592.98	455.51	381.59	483.38	336.29	0	393.19	--	447.84	369.65
1980--											
1st quarter	477.16	631.94	501.19	0	531.66	439.82	0	0	379.65	495.42	458.30
2d quarter	521.89	631.10	503.85	0	536.72	531.32	0	0	0	895.65	554.48
3d quarter	405.84	590.80	495.56	0	495.87	397.75	0	0	0	535.94	489.40
4th quarter	386.99	540.59	447.85	0	455.45	505.15	0	485.28	0	608.07	503.48
1980 average	452.99	604.08	488.22	0	508.23	462.98	0	485.28	379.65	535.17	492.37
1981--											
1st quarter	356.89	683.24	426.13	0	479.01	0	0	521.81	0	986.26	539.15
2d quarter											
3d quarter											
4th quarter											
1981 average											

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

<sup>1</sup>State averages as presented here for Washington and Oregon do not agree with those found in table 10 because customs districts as used in table 10 do not correspond to State boundaries.

YEAR AND QUARTER	VOLUME	AVERAGE VALUE
TO ALL COUNTRIES		
1970	51,531	125.58
1971	42,600	116.54
1972	65,837	125.88
1973	71,719	248.23
1974	34,949	240.82
1975	29,011	307.97
1976	26,197	224.59
1977	52,377	263.54
1978	68,025	320.45
1979	128,597	470.97
1980--		
1st quarter	26,021	475.33
2d quarter	44,334	501.91
3d quarter	58,369	537.30
4th quarter	31,799	613.44
1980 total and average value	160,523	532.56
1981--		
1st quarter	25,305	584.21
2d quarter		
3d quarter		
4th quarter		
1981 total and average value		
TO JAPAN		
1970	47,583	129.67
1971	38,948	120.94
1972	61,882	129.99
1973	71,705	248.24
1974	29,088	252.71
1975	24,311	352.29
1976	20,741	253.18
1977	46,897	278.99
1978	57,653	343.49
1979	120,753	475.21
1980--		
1st quarter	25,223	472.33
2d quarter	42,239	512.10
3d quarter	57,678	535.22
4th quarter	31,135	607.49
1980 total and average value	156,275	533.22
1981--		
1st quarter	24,979	507.25
2d quarter		
3d quarter		
4th quarter		
1981 total and average value		
TO MAINLAND CHINA		
1981--		
1st quarter	163	351.39
2d quarter		
3d quarter		
4th quarter		
1981 total and average value		

Source--U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Data are compiled from Department of Commerce records at the end of each quarter.

TO ALL COUNTRIES

1970	2,052	921,655	98	78,348	0	--	2,353	2,973,898
1971	786	681,962	192	245,213	0	--	1,275	1,643,951
1972	2,999	882,806	68	133,979	0	--	1,320	2,015,855
1973	1,812	1,351,759	36	57,747	0	--	1,084	2,330,761
1974	633	1,121,192	45	95,342	0	--	560	1,515,476
1975	1,599	637,455	73	103,519	0	--	3,911	780,853
1976	3,750	1,646,972	236	136,188	0	--	659	1,239,777
1977	2,735	2,117,386	189	87,839	0	--	1,396	2,751,996
1978	2,362	2,190,449	75	91,486	11	19,250	1,772	4,088,466
1979	2,597	2,216,256	341	420,741	138	253,716	1,272	3,049,981
1980--								
1st quarter	2,918	1,336,275	327	94,704	28	7,000	249	757,307
2d quarter	1,914	1,173,664	909	351,476	78	23,200	390	800,759
3d quarter	1,194	1,494,397	142	66,189	74	10,000	52	101,932
4th quarter	800	1,149,375	648	252,142	6	4,760	209	592,963

1980 total 6,826 5,153,711 2,026 764,511 186 44,960 900 2,260,961

1981--								
1st quarter	1,250	969,546	122	162,848	0	--	404	834,877
2d quarter								
3d quarter								
4th quarter								

1981 total

TO JAPAN

1970	1,672	889,649	96	75,855	0	--	2,296	2,935,506
1971	762	669,251	192	245,213	0	--	1,222	1,588,353
1972	1,374	727,475	64	130,080	0	--	1,126	1,761,797
1973	993	1,164,704	34	56,842	0	--	1,015	2,250,213
1974	540	1,063,245	37	84,293	0	--	485	1,093,502
1975	1,210	562,583	14	9,039	0	--	3,803	636,796
1976	3,313	1,416,317	235	134,988	0	--	456	1,005,649
1977	1,444	1,179,616	17	33,347	0	--	1,063	2,300,667
1978	1,178	819,332	57	84,025	0	--	1,248	3,059,204
1979	1,824	1,153,644	300	359,119	74	188,389	1,059	2,339,009
1980--								
1st quarter	2,714	826,696	316	87,867	28	7,000	182	602,583
2d quarter	1,552	749,394	906	344,457	78	23,200	206	468,706
3d quarter	149	113,210	134	57,889	74	10,000	51	100,732
4th quarter	371	279,945	608	236,678	2	2,000	140	360,475

1980 total 4,786 1,969,245 1,964 726,891 182 42,200 579 1,532,496

1981--								
1st quarter	287	393,303	117	146,848	0	--	224	574,714
2d quarter								
3d quarter								
4th quarter								

1981 total

TO MAINLAND CHINA

1980--								
1st quarter	--	--	--	--	--	--	--	--
2d quarter	6	2,800	--	--	--	--	--	--
3d quarter	--	--	--	--	--	--	--	--
4th quarter	--	--	--	--	--	--	--	--

1980 total 6 2,800 -- -- -- -- --

1981--								
1st quarter	0	--	0	--	0	--	0	--
2d quarter								
3d quarter								
4th quarter								

1981 total

Source--U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Data are compiled from Department of Commerce records at the end of each quarter. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. Alaska Customs District is the State of Alaska. San Francisco Customs District includes Monterey and all ports north of Monterey, California.

YEAR AND QUARTER	TOTAL	DOUGLAS- FIR	OTHER SOFTWOODS	HARDWOODS
1970	561	276	60	225
1971	365	90	84	191
1972	631	203	92	336
1973	445	214	5	226
1974	378	32	130	216
1975	288	11	224	53
1976	2,396	1,411	670	315
1977	1,360	169	411	780
1978	1,721	172	917	632
1979	2,117	290	359	1,468
1980--				
1st quarter	232	59	98	75
2d quarter	376	171	110	95
3d quarter	406	65	303	38
4th quarter	135	0	99	36
1980 total	1,149	295	610	244
1981--				
1st quarter	235	30	86	119
2d quarter				
3d quarter				
4th quarter				
1981 total				

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter. Revisions which may have been made after this time are not shown. Southern California consists of the San Diego and Los Angeles Customs Districts and includes all ports south of Monterey, California.

YEAR AND QUARTER	ALL SPECIES		DOUGLAS-FIR		OTHER SOFTWOODS	
	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE
1970	96	111.47	30	146.57	66	95.62
1971	853	103.53	0	--	853	103.53
1972	392	113.71	19	162.89	373	111.20
1973	379	177.58	93	261.16	286	150.40
1974	925	178.24	19	149.05	906	178.86
1975	739	226.93	72	274.78	667	221.76
1976	571	228.43	103	254.08	468	222.78
1977	1,227	247.66	467	251.10	760	245.54
1978	901	226.05	136	367.43	765	200.91
1979	3,906	168.47	0	--	3,906	168.47
1980--						
1st quarter	135	303.18	15	281.67	120	305.87
2d quarter	236	189.98	0	--	236	189.98
3d quarter	156	257.12	21	319.14	135	247.47
4th quarter	172	243.02	0	--	172	243.02
1980 total and average value	699	239.88	36	303.53	663	236.42
1981--						
1st quarter	141	446.81	123	475.06	18	253.78
2d quarter						
3d quarter						
4th quarter						
1981 total and average value						

Source--U.S. Department of Commerce. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Data are compiled from Department of Commerce records at the end of each quarter.

<sup>1</sup>Montana Customs District includes all ports in Montana and Idaho.



## TO ALL COUNTRIES

1970	269,201	4,209	90,266	59,641	61,192	51,660	2,233
1971	158,579	3,750	41,633	48,260	45,519	14,177	5,240
1972	55,866	836	13,956	18,477	14,958	3,965	3,674
1973	35,716	1,852	9,750	7,441	13,647	1,211	1,815
1974	148,801	11,790	31,528	67,843	27,355	4,973	5,312
1975	85,082	2,406	18,914	19,373	41,416	1,505	2,188
1976	116,193	5,390	39,069	21,901	41,959	3,346	4,528
1977	186,511	10,085	118,085	36,048	19,835	754	1,704
1978	128,853	8,592	24,467	45,143	49,767	530	354
1979	169,107	2,431	56,504	56,954	43,201	4,135	5,882
1980--							
1st quarter	41,753	0	14,899	11,096	9,341	1,864	4,553
2d quarter	45,863	6,177	14,830	6,688	9,950	3,482	4,736
3d quarter	94,870	1,687	52,201	19,681	11,246	6,676	3,379
4th quarter	49,298	1,043	24,263	12,125	6,219	133	5,515

1980 total 231,784 8,907 106,193 49,590 36,756 12,155 18,183

1981--

1st quarter NA NA NA NA NA NA NA  
 2d quarter  
 3d quarter  
 4th quarter

1981 total

## TO JAPAN

1970	140,502	2,833	39,338	30,100	54,642	21,479	110
1971	94,669	2,218	21,362	24,150	40,472	6,379	88
1972	46,059	567	13,478	13,412	14,938	3,664	0
1973	29,239	1,293	8,050	6,205	13,284	399	0
1974	80,655	2,167	22,968	31,915	16,503	2,304	4,798
1975	61,728	1,460	10,477	7,696	39,470	1,253	1,372
1976	67,192	792	17,026	7,343	39,905	470	1,656
1977	109,301	5,106	65,092	23,413	15,489	201	0
1978	90,001	4,094	16,890	24,038	44,814	99	66
1979	120,297	1,894	49,281	27,597	35,883	3,636	2,056
1980--							
1st quarter	31,167	0	9,479	7,701	9,336	1,515	3,136
2d quarter	27,348	303	5,234	6,436	9,950	2,800	2,625
3d quarter	65,015	576	34,851	13,563	10,637	2,491	2,897
4th quarter	31,294	813	11,936	7,646	6,234	133	4,532

1980 total 154,824 1,692 61,500 35,346 36,157 6,939 13,190

1981--

1st quarter NA NA NA NA NA NA NA  
 2d quarter  
 3d quarter  
 4th quarter

1981 total

## TO UNITED STATES

1970	120,698	1,376	50,928	29,540	6,550	30,181	2,123
1971	63,910	1,532	20,271	24,110	5,047	7,798	5,152
1972	9,807	269	478	5,065	20	301	3,674
1973	6,471	559	1,692	1,236	363	812	1,809
1974	68,146	9,623	8,560	35,920	10,852	2,669	514
1975	23,354	946	7,717	11,677	1,946	252	816
1976	40,911	4,598	22,043	14,558	1,964	2,876	2,872
1977	74,442	4,979	50,817	12,043	4,346	553	1,704
1978	32,843	4,498	6,039	19,144	2,443	431	288
1979	48,810	537	7,223	29,357	7,368	499	3,826
1980--							
1st quarter	10,581	0	5,420	3,395	0	349	1,417
2d quarter	18,515	5,874	9,596	752	0	682	2,111
3d quarter	29,770	1,111	17,350	6,048	594	4,185	482
4th quarter	18,089	230	12,327	4,549	0	0	983

1980 total 76,955 7,215 44,693 14,244 594 5,216 4,993

1981--

1st quarter NA NA NA NA NA NA NA  
 2d quarter  
 3d quarter  
 4th quarter

1981 total

Source--Bureau of Economics and Statistics, Department of Industrial Development, Trade, and Commerce, Victoria, B.C., "Preliminary Statement of External Trade."

Figures do not include shipments of pulpwood logs.

NA = not available.

thousand board feet)

YEAR AND QUARTER	VOLUME	AVERAGE VALUE
1970	99,462	82.57
1971	60,333	64.70
1972	8,451	80.44
1973	2,102	124.71
1974	31,625	248.69
1975	55,494	207.13
1976	44,438	122.62
1977	91,962	194.93
1978	41,307	271.29
1979	75,855	298.89
1980—		
1st quarter	9,115	341.27
2d quarter	8,377	319.09
3d quarter	15,486	233.34
4th quarter	18,850	142.33
1980 total and average value	51,828	233.08
1981—		
1st quarter	13,223	300.05
2d quarter		
3d quarter		
4th quarter		
1981 total and average value		

Source—U.S. Department of Commerce. Value is declared value at port of entry. Data are compiled from Department of Commerce records at the end of each quarter.

YEAR AND QUARTER	VOLUME	VALUE	VOLUME	VALUE
	<u>Short tons</u>	<u>Dollars</u>	<u>Cords</u>	<u>Dollars</u>
1970	795,044	8.44	17,501	NA
1971	1,157,444	9.57	3,944	19.47
1972	909,926	9.87	2,300	47.56
1973	1,085,124	11.19	16	97.06
1974	623,830	15.55	31,998	60.08
1975	493,761	23.36	11,517	42.90
1976	877,550	20.98	1,967	32.14
1977	1,056,102	18.59	16,674	91.19
1978	1,215,483	16.37	--	--
1979	1,039,458	17.19	--	--
1980--				
1st quarter	252,549	23.92	150	86.87
2d quarter	375,769	24.76	5,182	125.75
3d quarter	264,794	27.28	5,638	165.90
4th quarter	292,589	31.36	46,367	47.,0
1980 total and average value	1,185,701	26.77	57,337	66.64
1981--				
1st quarter	318,965	33.14	13,245	134.14
2d quarter				
3d quarter				
4th quarter				
1981 total and average value				

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

NA = not available.

YEAR AND QUARTER	WASHINGTON CUSTOMS DISTRICT		OREGON CUSTOMS DISTRICT		SAN FRANCISCO CUSTOMS DISTRICT		ALASKA CUSTOMS DISTRICT	
	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE
1970	238,757	19.56	1,605,062	19.31	267,347	NA	--	--
1971	229,237	17.87	1,504,169	20.94	476,400	NA	19,600	28.06
1972	168,725	19.56	2,081,032	22.12	253,401	27.76	20,158	25.76
1973	272,196	21.84	2,778,829	24.85	369,403	24.41	--	--
1974	390,370	28.62	3,177,465	26.50	242,017	30.69	34,828	28.99
1975	326,083	38.56	2,436,807	34.74	257,735	28.96	32,399	48.51
1976	457,801	33.39	2,881,577	39.90	366,678	34.76	107,652	37.89
1977	281,540	49.17	2,892,333	43.33	519,444	42.91	107,429	51.67
1978	299,140	46.16	2,650,423	42.98	412,107	40.82	31,827	37.20
1979	346,209	50.05	3,125,103	42.55	603,989	44.69	83,706	48.62
1980--								
1st quarter	21,508	56.29	737,661	63.71	134,188	63.84	30,649	83.49
2d quarter	123,993	76.67	767,411	85.88	236,482	66.31	57,860	49.94
3d quarter	31,697	91.79	716,415	109.10	214,926	114.01	40,103	97.34
4th quarter	90,905	84.65	628,440	97.05	142,863	96.28	22,716	91.76
1980 total and average value	268,103	79.53	2,849,927	88.44	728,459	85.81	151,328	75.57
1981--								
1st quarter	49,140	73.54	715,962	87.17	136,498	91.69	10,534	48.05
2d quarter								
3d quarter								
4th quarter								
1981 total and average value								

Source--U.S. Department of Commerce except for San Francisco data for 1970 and 1971 which were obtained from the Port of Sacramento. The valuation definition used in the export statistics is the value at the seaport or border port of exportation. It is based on the selling price (or cost if not sold) and includes inland freight, insurance, and other charges to the port of exportation. Washington Customs District includes all ports in the State of Washington, except Longview and Vancouver. Oregon Customs District includes all Oregon ports and Longview and Vancouver, Washington. San Francisco Customs District includes all coastal and inland ports in the State of California from Monterey north. The Alaska Customs District is the State of Alaska.

NA = not available.

## TO ALL COUNTRIES

1970	409,872	304,578	33,810	71,484	136,124	76,401	12,279	47,444	273,748	228,177	21,531	24,040
1971	334,318	267,429	22,344	44,545	130,186	88,532	9,902	31,752	204,132	178,897	12,442	12,793
1972	406,493	321,761	30,772	53,960	164,472	99,927	21,994	42,551	242,021	221,834	8,778	11,409
1973	799,631	532,321	169,927	97,383	324,740	143,666	104,851	76,223	474,891	388,655	65,076	21,160
1974	719,729	496,978	124,047	98,704	331,818	174,056	79,399	78,363	387,911	322,922	44,648	20,341
1975	616,883	415,152	125,529	76,202	263,754	151,681	52,064	60,009	353,129	263,471	73,465	16,193
1976	698,941	478,100	145,645	75,196	311,599	155,041	94,581	61,977	387,342	323,059	51,064	13,219
1977	549,059	372,609	125,479	50,971	256,703	123,783	92,364	40,556	292,356	248,826	33,115	10,415
1978	585,588	374,032	135,156	76,400	310,100	128,895	118,094	63,111	275,488	245,137	17,062	13,289
1979	839,895	427,063	280,067	132,765	413,673	98,685	211,030	103,858	426,322	328,378	69,031	28,907
1980--												
1st quarter	247,234	113,090	89,573	44,571	140,823	28,318	76,484	36,021	106,411	84,772	13,089	8,550
2d quarter	312,038	146,872	106,431	58,735	159,134	32,973	81,467	44,694	152,904	113,899	24,964	14,041
3d quarter	217,915	95,562	75,976	46,377	111,680	22,074	57,714	31,892	106,235	73,488	18,262	14,485
4th quarter	207,695	93,599	66,507	47,589	110,091	23,306	55,041	31,744	97,604	70,293	11,466	15,845

1980 total 984,882 449,123 338,487 197,272 521,728 106,671 270,706 144,351 463,154 342,452 67,781 52,921

1981--  
1st quarter 245,806 124,627 68,610 52,569 125,778 35,531 50,166 40,081 120,028 89,096 18,444 12,488  
2d quarter  
3d quarter  
4th quarter

1981 total

## TO JAPAN

1970	30,294	4,949	14,983	10,362	13,859	2,656	5,693	5,510	16,435	2,293	9,290	4,852
1971	16,736	3,252	7,080	6,404	12,816	2,239	5,610	4,967	3,920	1,013	1,470	1,437
1972	23,699	3,437	10,589	9,673	14,951	571	7,291	7,089	8,748	2,866	3,298	2,584
1973	153,537	40,402	99,707	13,428	89,514	19,247	64,966	5,301	64,023	21,155	34,741	8,127
1974	205,888	102,858	77,973	25,057	103,531	44,424	47,616	11,491	102,357	58,434	30,357	13,566
1975	208,160	96,307	96,610	15,243	89,489	40,991	45,359	3,139	118,671	55,316	51,251	12,104
1976	186,628	68,927	107,884	9,817	127,553	39,430	80,891	7,232	59,075	29,497	26,993	2,585
1977	145,306	40,945	93,719	10,722	108,468	20,845	80,161	7,462	36,918	20,100	13,558	3,260
1978	163,233	36,429	108,610	18,194	141,963	25,609	103,056	13,289	21,270	10,820	5,554	4,896
1979	355,840	75,567	227,702	52,571	258,444	45,549	177,239	35,656	97,396	30,018	50,463	16,915
1980--												
1st quarter	89,497	10,144	61,733	17,620	70,326	5,917	53,218	11,191	19,171	4,227	8,515	6,429
2d quarter	117,162	17,324	81,874	17,964	82,103	7,042	62,243	12,818	35,059	10,282R	19,631	5,146
3d quarter	88,436	16,380	50,701	13,355	62,808	7,793	44,347	10,668	25,620	8,587	14,354	2,687
4th quarter	67,363	9,236	47,421	10,706	54,169	5,676	39,429	9,064	13,194	3,560	7,992	1,642

1980 total 362,458 53,084 249,729 59,645 269,406 26,428 199,237 43,741 93,052 26,656 50,492 15,904

1981--  
1st quarter 82,390 17,199 51,779 13,412 55,324 9,201 36,658 9,465 27,066 7,998 15,121 3,947  
2d quarter  
3d quarter  
4th quarter

1981 total

## TO CANADA

1970	44,153	32,029	1,384	10,740	44,153	32,029	1,384	10,740	0	0	0	0
1971	46,618	32,989	1,339	12,290	46,618	32,989	1,339	12,290	0	0	0	0
1972	70,297	42,581	8,687	19,029	70,297	42,581	8,687	19,029	0	0	0	0
1973	88,695	49,381	9,340	29,974	88,695	49,381	9,340	29,974	0	0	0	0
1974	126,547	67,856	5,952	52,739	124,097	65,406	5,952	52,739	2,450	2,450	0	0
1975	113,713	61,099	4,299	47,815	112,783	61,099	3,869	47,815	430	0	430	0
1976	101,633	50,327	6,737	44,569	101,633	50,327	6,737	44,569	0	0	0	0
1977	76,251	45,842	3,695	26,714	76,251	45,842	3,695	26,714	0	0	0	0
1978	117,969	69,852	9,241	38,876	117,930	69,813	9,241	38,876	39	39	0	0
1979	113,977	38,917	18,870	56,190	113,977	38,917	18,870	56,190	0	0	0	0
1980--												
1st quarter	46,038	16,609	10,231	19,198	46,038	16,609	10,231	19,198	0	0	0	0
2d quarter	47,329	17,946	6,469	22,914	47,329	17,946	6,469	22,914	0	0	0	0
3d quarter	30,018	8,851	3,979	17,188	30,018	8,851	3,979	17,188	0	0	0	0
4th quarter	36,273	11,470	5,646	19,157	36,273	11,470	5,646	19,157	0	0	0	0

1980 total 159,658 54,876 26,325 78,457 159,658 54,876 26,325 78,457 0 0 0 0

1981--  
1st quarter 51,382 20,608 4,922 25,852 51,382 20,608 4,922 25,852 0 0 0 0  
2d quarter  
3d quarter  
4th quarter

1981 total

## TO MAINLAND CHINA

1981--												
1st quarter	441	359	0	82	82	0	0	82	359	359	0	0
2d quarter												
3d quarter												
4th quarter												

1981 total

Source—U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.  
Includes lumber classified as railroad cross ties and not specified by species.

TO ALL COUNTRIES

1970	52,681	26,645	8	26,028
1971	38,397	21,267	0	17,130
1972	48,914	20,843	135	27,936
1973	73,842	30,746	2,530	40,566
1974	35,314	17,350	815	17,149
1975	27,628	13,388	636	13,604
1976	40,585	14,430	462	25,693
1977	44,438	18,951	1,137	24,350
1978	32,919	12,931	684	19,304
1979	30,832	10,539	1,498	18,795
1980--				
1st quarter	7,934	1,780	354	5,800
2d quarter	13,118	6,385	849	5,884
3d quarter	6,983	1,167	1,360	4,456
4th quarter	6,568	1,199	1,214	4,155

1980 total	34,603	10,531	3,777	20,295
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1981--				
1st quarter	7,446	2,183	2,002	3,261
2d quarter				
3d quarter				
4th quarter				

1981 total

TO JAPAN

1970	8,472	48	0	8,424
1971	3,695	0	0	3,695
1972	6,884	17	28	6,839
1973	4,963	328	2,359	2,276
1974	3,208	317	12	2,879
1975	4,303	337	--	3,966
1976	5,724	168	396	5,160
1977	7,766	1,354	--	6,412
1978	6,763	107	200	6,456
1979	8,854	0	700	8,154
1980--				
1st quarter	4,173	58	274	3,841
2d quarter	4,188	306	716	3,166
3d quarter	4,431	574	1,052	2,805
4th quarter	4,592	222	1,214	3,156

1980 total	17,384	1,160	3,256	12,968
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1981--				
1st quarter	4,520	464	1,809	2,247
2d quarter				
3d quarter				
4th quarter				

1981 total

Source--U.S. Department of Commerce.

<sup>1</sup>Northern California consists of the San Francisco Customs District and includes Monterey, California, and all ports north of Monterey.

## TO ALL COUNTRIES

1970	45,405	18,751	26,654
1971	42,446	15,086	27,360
1972	56,599	23,938	32,661
1973	52,608	19,599	33,009
1974	46,514	18,684	27,830
1975	56,759	23,596	33,163
1976	61,256	23,078	38,178
1977	72,588	26,895	45,693
1978	74,347	27,661	46,686
1979	81,372	20,388	60,984
1980--			
1st quarter	17,551	3,970	13,581
2d quarter	25,062	6,220	18,842
3d quarter	25,754	6,251	19,503
4th quarter	27,274	8,389	18,885

1980 total	95,641	24,830	70,811
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1981--

1st quarter	24,137	5,252	18,885
2d quarter			
3d quarter			
4th quarter			

1981 total

## TO JAPAN

1970	--	--	--
1971	1,156	--	1,156
1972	1,578	12	1,566
1973	264	--	264
1974	64	--	64
1975	119	--	119
1976	377	--	377
1977	172	73	99
1978	471	--	471
1979	739	--	739
1980--			
1st quarter	180	--	180
2d quarter	284	20	264
3d quarter	760	--	760
4th quarter	1,106	217	889

1980 total	2,330	237	2,093
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1981--

1st quarter	490	68	422
2d quarter			
3d quarter			
4th quarter			

1981 total

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.

<sup>1</sup>Southern California consists of the San Diego and Los Angeles Customs Districts and includes all ports south of Monterey, California.

QUARTER	TOTAL	KOREA	SPRUE	CEBR	SEP PRODS
TO ALL COUNTRIES					
1970	315,586	90,974	219,001	708	4,893
1971	247,414	92,243	155,171	0	0
1972	340,196	155,407	184,649	0	140
1973	404,849	210,555	194,143	12	139
1974	362,432	250,144	154,525	2,641	122
1975	313,307	179,398	132,556	1,353	0
1976	290,011	134,387	148,526	1,298	5,800
1977	250,044	122,544	121,350	5,579	571
1978	237,795	126,218	111,435	53	89
1979	278,462	172,005	103,844	479	2,134
1980	256,716	158,682	96,607	105	1,322
1st quarter	66,402	43,514	22,888	0	0
2d quarter	84,526	52,75	31,669	105	0
3d quarter	58,537	33,638	24,221	0	678
4th quarter	47,251	28,778	17,829	0	644
1980 total	256,716	158,682	96,607	105	1,322
1981—					
1st quarter	54,446	22,644	31,802	0	0
2d quarter					
3d quarter					
4th quarter					

1981 total

TO JAPAN					
1970	315,386	90,774	219,011	708	4,893
1971	245,974	91,357	154,617	0	0
1972	336,798	152,555	184,243	0	0
1973	403,938	210,536	193,390	12	0
1974	361,691	204,845	154,205	2,641	0
1975	312,976	179,122	132,501	1,353	0
1976	289,197	134,274	148,221	902	5,800
1977	245,445	122,471	121,083	1,391	500
1978	236,615	125,355	111,207	53	0
1979	273,615	170,149	101,408	435	1,623
1980	251,369	156,654	94,610	105	0
1st quarter	63,403	41,507	21,896	0	0
2d quarter	84,505	52,731	31,669	105	0
3d quarter	56,854	33,638	23,216	0	0
4th quarter	46,607	28,778	17,829	0	0
1980 total	251,369	156,654	94,610	105	0
1981—					
1st quarter	41,731	18,861	22,870	0	0
2d quarter					
3d quarter					
4th quarter					

1981 total

TO MAINLAND CHINA					
1981—					
1st quarter	8,721	0	8,721	0	0
2d quarter					
3d quarter					
4th quarter					
1981 total					

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter.



YEAR AND QUARTER	TOTAL	DOUGLAS-FIR	WESTERN HEMLOCK	OTHER SOFTWOODS
1970	10,794	6,424	32	4,338
1971	12,417	4,660	800	6,957
1972	16,360	6,391	1,595	8,374
1973	47,727	30,526	3,334	13,867
1974	29,146	9,618	3,602	15,926
1975	50,226	12,745	4,516	32,965
1976	56,451	19,050	3,521	33,880
1977	46,488	12,660	3,463	30,365
1978	44,612	12,691	2,276	29,645
1979	81,671	22,067	1,632	57,972
1980--				
1st quarter	18,458	3,649	267	14,542
2d quarter	14,497	4,434	303	9,760
3d quarter	12,692	3,099	650	8,943
4th quarter	11,909	2,848	583	8,478
1980 total	57,556	14,030	1,803	41,723
1981--				
1st quarter	19,012	3,036	298	12,678
2d quarter				
3d quarter				
4th quarter				
1981 total				

Source--U.S. Department of Commerce.

<sup>1</sup>Montana Customs District includes all ports in Montana and Idaho.

TO ALL COUNTRIES

1970	3,461,067	706,323	1,838,779	362,799	419,746	131,291	2,129
1971	3,300,365	675,773	1,703,632	324,910	440,595	153,769	1,686
1972	3,834,552	707,112	1,801,818	406,409	634,563	278,836	5,814
1973	4,169,812	566,535	2,032,594	456,522	766,830	344,401	2,930
1974	3,938,940	527,706	1,699,277	406,419	914,787	387,043	3,708
1975	3,001,410	356,371	1,113,665	295,218	825,527	409,507	1,122
1976	4,670,033	542,197	1,967,446	467,829	1,191,429	499,853	1,279
1977	5,860,807	683,614	2,364,028	533,267	2,269,876	8,796	1,226
1978	5,876,119	679,566	2,492,764	570,796	2,116,258	15,674	1,061
1979	5,755,532	679,694	2,313,186	646,701	1,983,829	129,161	2,961
1980—							
1st quarter	1,319,721	113,019	571,697	170,973	442,955	20,322	755
2d quarter	1,647,910	118,785	544,037	462,851	498,880	22,988	369
3d quarter	1,348,984	155,116	487,292	218,542	462,354	24,691	989
4th quarter	1,244,185	111,505	495,646	135,981	468,045	31,623	1,385

1980 total 5,560,800 498,425 2,098,672 988,347 1,872,234 99,624 3,498

1981  
1st quarter NA NA NA NA NA NA NA  
2d quarter  
3d quarter  
4th quarter

1981 total

TO JAPAN

1970	727,599	29,489	549,554	94,828	53,726	2	0
1971	419,819	14,181	305,535	44,221	54,136	1,668	78
1972	400,051	15,268	300,460	46,052	34,003	526	3,742
1973	617,449	12,987	441,852	88,946	71,531	1,849	284
1974	500,785	15,335	349,560	83,749	49,116	2,490	535
1975	407,674	12,870	301,336	60,490	30,488	2,405	85
1976	633,863	13,727	476,927	79,934	61,743	1,521	11
1977	705,823	18,530	530,567	90,447	65,943	85	251
1978	779,135	23,799	545,983	116,368	92,940	0	45
1979	1,014,481	44,021	677,425	158,121	133,358	546	1,010
1980—							
1st quarter	286,101	10,072	184,803	46,690	43,556	660	320
2d quarter	311,989	15,219	198,571	46,185	51,682	273	59
3d quarter	293,144	18,325	184,280	35,324	54,578	527	110
4th quarter	193,192	12,184	133,925	7,931	35,563	2,698	891

1980 total 1,084,426 55,800 701,579 136,130 185,379 4,158 1,300

1981—  
1st quarter NA NA NA NA NA NA NA  
2d quarter  
3d quarter  
4th quarter

1981 total

TO UNITED STATES<sup>1</sup>

1970	1,627,613	401,167	768,772	137,361	202,152	116,032	2,129
1971	2,163,431	502,631	1,028,356	203,577	285,343	141,943	1,581
1972	2,679,159	505,902	1,155,419	254,521	491,717	270,079	2,071
1973	2,601,556	347,653	1,143,329	240,978	544,634	322,316	2,646
1974	2,207,461	302,112	761,924	207,138	659,751	353,487	3,049
1975	2,026,343	238,331	542,256	166,949	684,404	393,391	1,012
1976	2,965,011	322,793	978,784	267,831	938,185	456,237	1,181
1977	4,107,653	529,808	1,340,920	333,604	1,894,371	7,988	962
1978	4,078,666	501,841	1,443,548	365,062	1,751,741	15,496	978
1979	3,528,648	462,658	1,125,807	382,991	1,479,014	126,536	1,642
1980—							
1st quarter	637,007	58,070	217,757	96,434	244,783	19,544	419
2d quarter	609,932E	58,994	166,082	93,966E	267,947	22,636	307
3d quarter	591,133E	98,469	138,128	69,453E	260,570	23,645	868
4th quarter	752,814	67,949	253,460	95,966	306,087	28,058	494

1980 total 2,590,886 283,482 775,427 355,819 1,079,387 94,683 2,088

1981—  
1st quarter NA NA NA NA NA NA NA  
2d quarter  
3d quarter  
4th quarter

1981 total

Source—Bureau of Economics and Statistics, Department of Industrial Development, Trade, and Commerce, Victoria, B.C., "Preliminary Statement of External Trade."

<sup>1</sup>Figures do not include shipments of railroad crossties.

E = estimated.

NA = not available.

YEAR AND QUARTER	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE
TO ALL COUNTRIES						
1970	89,946	887	10,587	812	79,359	75
1971	71,479	1,314	11,247	1,035	60,232	279
1972	122,242	3,603	23,241	3,342	99,001	261
1973	284,806	6,337	45,493	5,546	239,313	791
1974	284,487	6,590	131,317	5,604	153,170	986
1975	407,117	10,493	93,951	10,360	313,166	133
1976	532,576	24,229	34,020	23,846	498,556	383
1977	233,762	17,673	20,603	17,447	213,159	226
1978	242,105	12,160	23,284	8,871	218,821	3,289
1979	330,018	9,962	27,132	9,644	302,886	318
1980--						
1st quarter	89,009	2,786	3,445	2,066	85,564	720
2d quarter	100,285	3,164	8,686	3,078	91,599	86
3d quarter	40,098	2,356	3,916	2,304	36,182	52
4th quarter	49,611	1,412	4,700	1,358	44,911	54
1980 total	279,003	9,718	20,747	8,806	258,256	912
1981--						
1st quarter	90,409	2,824	8,391	2,566	82,018	258
2d quarter						
3d quarter						
4th quarter						
1981 total						
TO JAPAN						
1970	998	2	525	2	473	0
1971	1,369	28	633	28	736	0
1972	734	34	432	0	302	34
1973	8,139	247	1,625	0	6,514	247
1974	3,311	188	1,203	11	2,108	177
1975	2,141	14	414	0	1,727	14
1976	2,361	61	498	61	1,863	0
1977	1,914	162	122	74	1,792	88
1978	2,821	18	167	18	2,654	0
1979	6,040	108	931	108	5,109	0
1980--						
1st quarter	838	4	270	4	568	0
2d quarter	5,134	85	3,158	85	1,976	0
3d quarter	1,386	889	443	889	943	0
4th quarter	943	0	287	0	656	0
1980 total	8,301	978	4,158	978	4,143	0
1981--						
1st quarter	1,294	4	581	3	713	1
2d quarter						
3d quarter						
4th quarter						
1981 total						

Source--U.S. Department of Commerce. Oregon Customs District includes all Oregon ports plus Longview and Vancouver, Washington. Washington Customs District includes all coastal and inland ports in the State of Washington, except Longview and Vancouver. Data are compiled from Department of Commerce records at the end of each quarter.

## NORTHERN CALIFORNIA

## SOUTHERN CALIFORNIA

YEAR AND QUARTER	TOTAL	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE	SOFTWOOD, 3/8-INCH BASIS	HARDWOOD, SURFACE MEASURE
1970	8,593	4,338	373	3,231	651
1971	11,440	4,303	139	5,896	1,102
1972	15,429	6,633	668	5,941	2,187
1973	16,562	8,186	698	4,358	3,320
1974	18,177	4,985	305	7,978	4,909
1975	19,619	7,874	542	6,311	4,892
1976	19,696	10,085	92	4,681	5,111
1977	9,198	5,148	646	1,818	1,586
1978	6,036	2,833	899	964	1,340
1979	5,934	1,638	871	1,946	1,479
1980--					
1st quarter	1,678	384	208	591	495
2d quarter	2,426	261	71	1,169	925
3d quarter	2,260	279	477	779	725
4th quarter	2,690	490	93	1,007	1,100
1980 total	9,054	1,414	849	3,546	3,245
1981--					
1st quarter	1,811	463	114	433	801
2d quarter					
3d quarter					
4th quarter					
1981 total					

Source--U.S. Department of Commerce. Data are compiled from Department of Commerce records at the end of each quarter. Revisions which may have been made after this time are not shown. Northern California is the San Francisco Customs District and includes all coastal and inland ports from Monterey north. Southern California consists of the San Diego and Los Angeles Customs Districts and includes all ports south of Monterey, California.

AGENCY	1976	1977	1978	1979	TOTAL	1ST QTR.	1ST QTR.	2D QTR.	3D QTR.	4TH QTR.	TOTAL
<hr/>											
Western Washington:											
U.S. Forest Service <sup>1/</sup>	883,213	1,066,656	1,097,548	1,222,548	1,114,024	217,198	202,579				
U.S. Bur. Indian Affairs	18,300	17,036	66,923	22,882	6,927	4,673	0				
State of Washington <sup>2/</sup>	690,015	746,012	175,155	1,150,935	503,565	248,970	115,505				
Total	1,591,528	1,829,764	1,339,675	2,396,365	1,624,516	470,841	318,084				
<hr/>											
Eastern Washington:											
U.S. Forest Service <sup>1/</sup>	247,937	271,698	382,902	420,819	428,631	92,031	63,187				
U.S. Bur. Land Manage.	3,058	2,768	54	2,645	1,798	0	0				
U.S. Bur. Indian Affairs	351,112	301,161	157,396	140,247	211,205	59,022	18,403				
State of Washington <sup>2/</sup>	82,138	82,828	30,385	125,505	80,345	38,665	9,480				
Total	684,245	658,455	570,737	689,216	721,979	189,718	91,070				
<hr/>											
Western Oregon:											
U.S. Forest Service <sup>1/</sup>	1,600,311	2,212,654	2,242,355	2,441,324	2,643,716	936,343	787,221				
U.S. Bur. Land Manage.	1,021,277	1,129,753	1,110,451	889,797	1,150,026	292,004	306,784				
State of Oregon	195,124	221,030	210,353	219,378	238,931	28,850	67,111				
Total	2,816,712	3,563,437	3,563,159	3,550,499	4,032,673	1,257,197	1,161,116				
<hr/>											
Eastern Oregon:											
U.S. Forest Service <sup>1/</sup>	896,293	1,127,107	1,115,280	1,271,677	1,168,327	306,828	309,238				
U.S. Bur. Land Manage.	3,864	11,788	12,152	6,525	2,301	415	8				
U.S. Bur. Indian Affairs	96,063	110,148	152,320	15,439	25,480	0	0				
State of Oregon	0	880	8,379	7,499	5,992	0	1,040				
Total	996,220	1,249,923	1,288,131	1,301,140	1,202,100	307,243	310,286				
<hr/>											
All public lands:											
U.S. Forest Service <sup>1/</sup>	3,627,754	4,678,115	4,838,134	5,356,368	5,354,698	1,552,400	1,362,225				
U.S. Bur. Land Manage.	1,028,199	1,144,309	1,122,657	898,967	1,154,125	292,419	306,792				
U.S. Bur. Indian Affairs	465,475	428,345	376,639	178,568	243,612	63,695	18,403				
State of Washington <sup>2/</sup>	772,153	828,900	205,540	1,276,440	583,910	287,635	124,985				
State of Oregon	195,124	221,910	218,732	226,877	244,923	28,850	68,151				
Total	6,088,705	7,301,579	6,761,702	7,937,220	7,581,268	2,224,999	1,880,556				

Source--respective agencies listed.

<sup>1</sup>Convertible products only.

<sup>2</sup>Excludes sales under \$2,000.

AGENCY	1976	1977	1978	1979	AVERAGE	1st QTR.	2nd QTR.	3rd QTR.	4th QTR.	AVERAGE
Western Washington:										
U.S. Forest Service <sup>1/</sup>	93.54	106.12	129.57	224.68	208.06	232.76	235.69			
U.S. Bur. Indian Affairs	120.88	163.54	120.34	264.95	182.32	211.07	0			
State of Washington <sup>2/</sup>	159.27	159.89	231.31	332.10	304.71	349.71	234.09			
Average	122.35	128.58	142.84	276.66	237.91	294.38	235.11			
Eastern Washington:										
U.S. Forest Service <sup>1/</sup>	39.45	56.36	186.69	104.68	90.92	115.07	64.56			
U.S. Bur. Land Manage.	69.71	77.02	123.48	16.80	21.25	--	--			
U.S. Bur. Indian Affairs	79.81	91.74	165.37	212.01	162.32	182.27	159.70			
State of Washington <sup>2/</sup>	101.19	107.39	162.13	210.79	207.67	211.16	276.21			
Average	67.71	79.10	179.49	145.50	124.63	155.56	105.78			
Western Oregon:										
U.S. Forest Service <sup>1/</sup>	141.54	181.51	210.96	332.09	354.60	384.23	358.34			
U.S. Bur. Land Manage.	157.74	180.82	196.36	292.69	323.63	353.50	309.79			
State of Oregon	146.11	172.37	226.23	314.93	332.25	308.35	315.67			
Average	147.73	180.73	207.31	321.13	344.44	375.35	343.05			
Eastern Oregon:										
U.S. Forest Service <sup>1/</sup>	65.66	109.58	171.04	169.55	130.22	169.31	179.61			
U.S. Bur. Land Manage.	54.33	99.54	206.17	103.25	118.72	115.66	245.62			
U.S. Bur. Indian Affairs	69.11	91.52	113.72	196.29	266.61	--	0			
State of Oregon	--	113.64	134.91	229.38	186.29	--	16.00			
Average	65.93	107.90	164.36	169.88	133.37	169.24	179.75			
All public lands:										
U.S. Forest Service <sup>1/</sup>	104.13	139.73	181.49	251.12	254.06	304.60	285.90			
U.S. Bur. Land Manage.	157.09	179.73	196.46	290.41	322.75	353.16	310.49			
U.S. Bur. Indian Affairs	79.22	94.54	136.48	217.43	173.80	184.38	159.70			
State of Washington <sup>2/</sup>	153.09	154.68	221.08	320.17	291.35	331.09	237.28			
State of Oregon	146.11	172.14	222.73	312.10	328.68	308.25	311.09			
Average	118.72	146.03	184.01	267.66	267.21	311.02	286.36			

Source--respective agencies listed.

<sup>1</sup>Prices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, quality, road costs, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest stumpage prices include deposits for sale-area betterment.

<sup>2</sup>Excludes sales under \$2,000.

Table 32—Average stumpage prices for sawtimber sold on National Forests by selected species, Pacific Northwest Region, 1970-81<sup>1</sup>  
(In dollars per thousand board feet)

YEAR AND QUARTER	DOUGLAS-FIR		PONDEROSA AND JEFFREY PINES	SUGAR PINE	WHITE PINE	LODGEPOLE PINE	ENGELMANN SPRUCE	SITKA SPRUCE	WESTERN HEMLOCK	CEDARS <sup>2</sup>	LARCH	NOBLE FIR AND SHASTA RED FIR	OTHE TRUE FIRS
	WEST SIDE	EAST SIDE											
1970	41.90	8.40	20.30	30.00	37.30	4.20	3.90	11.70	20.50	14.70	10.90	15.10	11.80
1971	49.10	4.40	22.30	23.10	22.30	5.20	8.00	18.10	20.60	17.20	5.30	24.60	12.20
1972	71.70	15.60	38.40	26.00	35.80	10.60	27.20	28.00	49.00	67.50	13.50	100.20	33.00
1973	138.10	60.40	77.70	60.50	50.70	38.40	55.60	93.40	99.20	146.80	53.90	81.40	73.80
1974	202.40	68.20	110.60	139.10	121.00	25.70	50.20	72.60	110.80	217.00	11.00	136.20	80.90
1975	169.50	34.30	43.10	109.90	84.40	15.40	13.70	75.90	68.50	119.20	5.80	117.70	45.10
1976	176.20	38.60	79.40	118.90	116.00	40.20	10.50	83.10	78.10	160.30	20.30	105.60	55.00
1977	225.90	71.20	138.40	162.80	142.70	35.40	36.50	103.00	89.20	149.60	62.10	128.90	85.10
1978	250.31	98.50	218.70	207.90	123.70	41.60	85.40	109.50	111.70	206.60	56.40	122.50	99.10
1979	394.30	81.70	238.00	267.30	181.90	47.10	51.60	227.90	197.10	329.10	90.50	211.30	189.80
1980—													
1st quarter	489.80	105.10	204.00	280.00	139.20	60.60	48.60	325.30	202.90	378.90	33.30	251.90	205.00
2d quarter	373.00	47.20	185.40	153.60	133.20	23.10	26.80	584.50	226.90	179.00	17.30	287.30	185.40
3rd quarter	400.30	53.90	170.30	115.30	55.60	43.40	22.20	251.80	218.90	148.40	53.30	232.50	142.50
4th quarter	458.20	84.50	32.20	147.00	92.70	43.80	42.50	86.20	151.80	609.88	4.40	180.32	132.80
1980 average	432.20	70.80	190.80	167.00	102.80	44.60	34.20	306.50	208.00	301.00	43.60	241.80	167.90
1981—													
1st quarter	465.40	136.10	262.60	186.60	79.50	76.10	4.60	153.90	170.40	160.40	17.30	120.60	99.40
2d quarter													
3d quarter													
4th quarter													
1981 average													

Source—Forest Service, U.S. Department of Agriculture. Pacific Northwest Region includes Oregon and Washington.

<sup>1</sup>Includes bid price plus deposits for sale-area betterment.

<sup>2</sup>Includes Port-Orford-cedar.

	WEST SIDE		EAST SIDE									
	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE	VOLUME	VALUE
Western Oregon:												
Mount Hood	40,070	461.08	13,700	315.91	2,100	13.45	22,540	139.28	5,860	133.85	99,321	294.97
Rogue River	12,930	245.61	0	0	80	83.11	125	275.00	11,140	194.60	33,680	220.55
Siskiyou	53,458	584.80	0	0	0	0	960	18.12	140	9.15	63,662	523.91
Siuslaw	164,660	444.38	0	0	0	0	16,986	187.79	0	0	192,240	403.16
Umpqua	77,420	445.54	0	0	700	128.60	5,700	60.07	4,510	27.56	116,535	313.80
Willamette	196,469	493.53	0	0	0	0	30,361	117.61	90	104.96	290,440	349.46
Total and average	545,007	472.55	13,700	315.91	2,880	43.38	76,672	134.26	21,740	142.00	795,878	358.91
Western Washington:												
Gifford Pinchot	18,900	582.41	0	0	0	0	2,200	27.80	6,600	12.58	29,670	378.09
Mount Baker-Snoqualmie	20,300	358.33	0	0	0	0	24,601	228.38	28,660	158.68	91,856	211.67
Olympic	25,135	270.79	0	0	0	0	41,345	242.38	2,000	65.56	77,915	221.42
Total and average	64,335	389.76	0	0	0	0	68,146	230.40	37,260	127.80	199,441	240.23
Total and average, western Oregon and western Washington	609,342	463.81	13,700	315.91	2,880	43.38	144,818	179.50	59,000	133.03	995,319	335.13
Eastern Oregon:												
Deschutes	0	0	3,310	6.70	26,047	332.30	0	0	3,180	21.42	47,177	192.83
Fremont	0	0	0	0	18,400	296.02	0	0	6,900	22.69	30,106	230.49
Malheur	0	0	9,400	48.90	36,850	221.74	0	0	7,150	13.28	66,800	148.88
Ochoco	0	0	0	0	0	0	0	0	0	0	0	0
Umatilla	0	0	7,400	171.95	16,200	179.07	0	0	4,500	17.20	30,000	142.99
Walla-Whitman	0	0	10,000	53.87	7,035	23.34	0	0	5,300	207.69	54,520	34.06
Winema	0	0	4,250	889.34	52,500	345.01	0	0	17,450	95.56	76,690	307.54
Total and average	0	0	34,360	176.74	157,032	276.70	0	0	44,480	71.16	305,293	182.49
Eastern Washington:												
Colville	0	0	8,055	124.62	0	0	0	0	1,200	14.93	12,275	106.05
Okanogan	0	0	18,421	14.62	7,529	104.91	0	0	0	0	25,950	40.82
Wenatchee	0	0	10,795	19.50	5,161	282.95	0	0	4,852	6.31	22,594	76.07
Total and average	0	0	37,271	39.80	12,690	177.32	0	0	6,052	8.02	60,819	67.08
Total and average, eastern Oregon and eastern Washington	0	0	71,631	105.49	169,722	269.27	0	0	50,532	63.60	366,112	163.32
Total and average, Region 6	609,342	463.81	85,331	139.27	172,602	265.50	144,818	179.50	109,532	101.00	1,361,431	288.93
Total and average, Oregon	545,007	472.55	48,060	216.41	159,912	272.50	76,672	134.26	66,220	94.41	1,101,171	310.00
Total and average, Washington	64,335	389.76	37,271	39.80	12,690	117.32	68,146	230.40	43,312	111.06	260,260	199.77

Source—U.S. Department of Agriculture. Pacific Northwest Region includes Oregon and Washington.

1Preliminary.



Table 34--Volume of timber sold on publicly owned or managed lands, Montana and Idaho, 1976-81  
(In thousand board feet, Scribner scale)

AGENCY	1980				1981				
	1976	1977	1978	1979	TOTAL	1ST QTR.	2D QTR.	3D QTR.	4TH QTR.
Montana:									
U.S. Forest Service <sup>1/</sup>	438,311	543,216	533,161	512,023	579,943	46,352			88,970
U.S. Bur. Land Manage. <sup>2/</sup>	3,401	3,730	4,576	9,148	11,079	982			312
U.S. Bur. Indian Affairs	6,558	147,917	6,880	37,468	25,405	14,424			5,677
State of Montana	18,675	20,842	25,036	28,110	24,662	8,517			9,425
Total	466,945	715,705	569,653	586,749	641,089	70,275			104,384
Idaho:									
U.S. Forest Service <sup>1/</sup>	622,131	783,631	836,629	843,992	828,507	117,129			171,166
U.S. Bur. Land Manage. <sup>2/</sup>	2,475	16,090	27,656	778	19,283	4,694			464
U.S. Bur. Indian Affairs	3,473	13,534	8,491	1,609	2,381	0			0
State of Idaho	97,178	124,325	120,261	179,307	222,137	52,397			1,170
Total	725,257	937,580	993,039	1,025,686	1,072,308	174,220			172,800
All public lands:									
U.S. Forest Service <sup>1/</sup>	1,060,442	1,326,847	1,369,790	1,356,0151	1,408,405	163,481			260,136
U.S. Bur. Land Manage. <sup>2/</sup>	5,876	19,820	32,232	9,926	30,362	5,676			776
U.S. Bur. Indian Affairs	10,031	161,451	15,371	39,077	27,786	14,424			5,677
State of Montana	18,675	20,845	25,036	28,110	24,662	8,517			9,425
State of Idaho	97,178	124,325	120,261	179,307	222,137	52,397			1,170
Total	1,192,202	1,653,285	1,562,690	1,612,435	1,713,397	244,495			277,184

Source--respective agencies listed.

<sup>1/</sup>Convertible products only.

<sup>2/</sup>Does not include cull log sales.

Table 35--Average stumpage prices of timber sold on publicly owned or managed lands, Montana and Idaho, 1976-81  
(In dollars per thousand board feet)

AGENCY	1976	1977	1978	1979	1980			1981		
					AVERAGE	1ST QTR.	2D QTR.	3D QTR.	4TH QTR.	AV
Montana:										
U.S. Forest Service <sup>1/</sup>	37.66	57.21	62.12	59.66	43.31	52.43		51.69		
U.S. Bur. Land Manage. <sup>2/</sup>	40.63	62.01	50.25	41.99	60.39	26.70		33.19		
U.S. Bur. Indian Affairs	55.51	24.93	35.78	114.61	104.81	131.69		59.13		
State of Montana	69.21	82.70	104.76	114.36	79.44	92.14		98.94		
Average	39.19	51.31	63.58	65.52	47.43	75.16		56.31		
Idaho:										
U.S. Forest Service <sup>1/</sup>	24.60	33.08	52.10	63.56	40.74	43.03		41.58		
U.S. Bur. Land Manage. <sup>2/</sup>	48.53	62.28	83.46	63.70	47.09	114.61		30.49		
U.S. Bur. Indian Affairs	39.97	82.38	67.51	119.89	129.09	--		--		
State of Idaho	69.01	82.26	133.14	102.23	92.21	86.67		62.41		
Average	30.71	40.81	62.92	70.41	51.71	58.08		41.69		
All public lands:										
U.S. Forest Service <sup>1/</sup>	30.00	42.96	56.00	62.09	41.80	45.70		45.04		
U.S. Bur. Land Manage. <sup>2/</sup>	43.96	62.23	78.75	43.69	51.94	99.41		31.58		
U.S. Bur. Indian Affairs	50.13	29.75	53.31	114.83	106.53	131.69		59.13		
State of Montana	69.21	82.70	104.76	114.36	79.44	92.14		98.94		
State of Idaho	69.01	82.26	133.14	102.23	92.21	86.67		62.41		
Average	34.03	45.35	63.16	68.63	50.11	62.37		47.20		

Source--respective agencies listed.

<sup>1</sup>Prices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, quality, road costs, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest stumpage prices include deposits for sale-area betterment.

<sup>2</sup>Does not include cull log sales.

Table 36—Average stumpage prices for sawtimber sold on National Forests by selected species, Northern Region, 1970-81<sup>1</sup>  
(In dollars per thousand board feet)

YEAR AND QUARTER	DOUGLAS- FIR	PONDEROSA PINE	WESTERN WHITE PINE	LODGEPOLE PINE	ENGELMANN SPRUCE	WESTERN HEMLOCK	CEDARS	LARCH	TRUE FIRS
1970	7.50	19.10	28.00	4.10	9.00	1.70	10.20	10.40	4.80
1971	10.10	11.20	23.00	8.30	13.30	2.90	9.10	17.30	4.90
1972	26.70	35.50	30.30	16.50	27.00	12.90	28.50	34.30	19.20
1973	50.70	66.50	65.90	38.30	65.80	42.60	45.20	66.30	46.10
1974	31.90	63.50	117.80	19.40	39.10	28.90	26.50	38.90	29.20
1975	14.40	22.40	36.20	19.20	10.90	2.00	42.50	20.30	4.80
1976	23.00	56.80	91.40	16.70	42.20	9.60	45.80	52.90	9.30
1977	41.50	96.60	122.70	38.30	61.40	11.90	72.00	72.20	20.20
1978	41.20	113.50	146.00	44.70	85.80	42.50	144.90	69.60	37.30
1979	51.90	127.20	185.60	34.40	75.90	62.10	117.20	91.40	43.90
1980	20.50	112.70	80.10	42.70	44.10	171.80	123.20	73.80	30.10
1981—									
1st quarter	22.90	51.10	92.70	53.80	123.30	58.90	103.50	32.50	87.30
2d quarter									
3d quarter									
4th quarter									
1981 average									

Source—Forest Service, U.S. Department of Agriculture. Northern Region includes Montana, northeastern Washington, northern Idaho, Dakota, and northwestern South Dakota.

<sup>1</sup>Includes bid price plus deposits for sale-area betterment.

Table 37--Volume of timber sold on publicly owned or managed lands in Alaska, 1976-81  
(In thousand board feet, Scribner scale)

AGENCY	1980					1981			
	1976	1977	1978	1979	TOTAL	1ST QTR.	2D QTR.	3D QTR.	4TH QTR.
U.S. Forest Service <sup>1/</sup>	15,619	80	175,140	93,733	145,285	468	14,066		
U.S. Bur. Land Manage. <sup>2/</sup>	215	54	142	22	125	0	0		
U.S. Bur. Indian Affairs	0	0	440	258,360	12,794	1,806	0		
State of Alaska	2,358	2,412	6,932	156,235	4,949	1,851	3,340		
Total	18,192	2,546	182,654	508,350	163,153	4,125	17,406		

Source--respective agencies listed.

<sup>1/</sup>Convertible products only.

<sup>2/</sup>Does not include cull log sales or volume given away through free use permits.

Table 38--Average stumpage prices of timber sold on publicly owned or managed lands in Alaska, 1976-81  
(In dollars per thousand board feet)

AGENCY	1976	1977	1978	1979	1980		1981	
					AVERAGE	1ST QTR.	1ST QTR.	2D QTR. 3D QTR.
U.S. Forest Service <sup>1/</sup>	25.34	63.00	51.73	159.71	101.72	8.79	37.11	
U.S. Bur. Land Manage. <sup>2/</sup>	20.00	9.17	94.72	34.09	6.00	--	--	
U.S. Bur. Indian Affairs	--	--	80.00	5.31	151.83	147.84	--	
State of Alaska	21.72	32.96	26.60	3.22	24.63	14.46	18.08	
Average	24.81	33.37	50.88	33.14	103.24	72.21	33.46	

Source--respective agencies listed. Includes products other than sawtimber.

<sup>1</sup>Prices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, costs, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest sales include deposits for sale-area betterment and are for convertible products only.

<sup>2</sup>Does not include cull log sales or volume given away through free use permits.

YEAR AND QUARTER	SITKA SPRUCE	WESTERN HEMLOCK	CEDAR AND OTHER SPECIES	ALL SPECIES
1970	21.40	7.70	47.80	12.90
1971	13.30	2.20	20.90	6.20
1972	7.30	7.90	1.00	7.60
1973	13.30	11.50	21.10	12.50
1974	41.80	22.30	41.70	28.80
1975	33.00	18.10	60.70	23.20
1976	25.10	12.00	67.30	28.00
1977	65.00	65.00	4.00	63.00
1978	99.17	4.27	136.17	40.57
1979	289.50	100.00	161.70	142.70
1980--				
1st quarter	7.90	5.80	15.00	8.10
2d quarter	58.70	7.60	25.20	28.80
3d quarter	215.70	18.50	461.50	102.30
4th quarter	0	0	0	0
1980 average	213.30	18.40	437.40	101.10
1981--				
1st quarter	168.10	2.00	45.30	36.80
2d quarter				
3d quarter				
4th quarter				
1981 average				

Source--Forest Service, U.S. Department of Agriculture. Alaska Region is the State of Alaska.

Table 40--Volume of timber sold on publicly owned or managed lands in California, 1976-81  
(In thousand board feet, Scribner scale)

AGENCY	1980					1981			
	1976	1977	1978	1979	TOTAL	1ST QTR.	2D QTR.	3D QTR.	4TH QTR.
U.S. Forest Service <sup>1/</sup>	1,443,372	1,716,954	2,001,607	2,071,263	1,875,796	358,862R	280,004		
U.S. Bur. Land Manage. <sup>2/</sup>	18,769	15,326	13,107	4,195	17,203	2,444	1,872		
U.S. Bur. Indian Affairs	30,428	28,580	37,200	33,729	22,230	11,730	0		
State of California	39,150	13,317	27,333	21,833	30,328	13,382	0		
Total	1,531,719	1,774,177	2,079,247	2,131,020	1,945,557	386,418R	281,876		

Source--respective agencies listed.

<sup>1/</sup>Convertible products only. Includes all of the Pacific Southwest Region and the portion of the Pacific Northwest Region in California.

<sup>2/</sup>Does not include cull log sales or volume given away through free use permits.

R = revised.

Table 1. Average stumpage prices of timber sold on publicly owned or managed lands in California, 1976-81  
(In dollars per thousand board feet)

AGENCY	1976	1977	1978	1979	1980				1981			
					Average	1ST QTR.	1ST QTR.	1ST QTR.	1ST QTR.	2D QTR.	3D QTR.	4TH QTR.
U.S. Forest Service <sup>1/</sup>	77.65	118.14	145.57	201.08	241.39	223.66R	207.16					
U.S. Bur. Land Manage. <sup>2/</sup>	71.35	150.92	96.39	102.59	173.25	134.44	169.86					
U.S. Bur. Indian Affairs	111.02	132.22	125.34	157.70	158.28	154.05	--					
State of California	142.04	137.13	273.35	370.76	283.94	339.12	--					
Average	79.88	118.80	146.58	201.94	240.51	224.99R	206.92					

Source--respective agencies listed.

<sup>1/</sup>Prices received for individual sales may vary significantly from the averages shown in this table because of differences in species mix, quality, costs, logging and processing costs, size and length of sale, number of bidders, and other related price determinants. National Forest stumpage prices include deposits for sale-area betterment.

<sup>2/</sup>Does not include cull log sales or volume given away through free use permits.  
R = revised.



YEAR AND QUARTER	DOUGLAS- FIR	PONDEROSA AND JEFFREY PINES	SUGAR PINE	LODGEPOLE PINE	CEDARS	TRUE FIRS	ALL SPECIES
1970	25.60	32.20	38.60	3.70	14.00	4.20	32.00
1971	27.50	33.00	46.40	2.40	30.30	7.10	26.00
1972	40.70	65.80	66.60	5.40	50.10	30.20	47.40
1973	84.80	108.60	89.30	12.40	86.40	70.20	83.10
1974	87.00	101.40	104.00	6.50	112.00	41.70	81.80
1975	51.40	71.00	99.00	22.40	79.90	19.70	53.80
1976	76.00	101.80	185.00	6.50	84.00	23.40	80.40
1977	124.30	131.40	168.50	165.20	337.90	50.60	121.10
1978	131.10	164.70	169.20	136.20	516.40	79.80	148.10
1979	186.60	239.00	375.40	25.40	497.10	96.00	206.20
1980--							
1st quarter	209.50	199.70	476.80	541.80	784.50	87.40	227.50
2d quarter	101.80	173.50	511.20	274.10	648.90	56.90	195.20
3d quarter	181.70	231.70	804.90	20.20	518.20	185.10	288.40
4th quarter	360.40	140.20	452.20	59.90	120.00	55.80	201.00
1980 average	189.50	206.10	671.40	252.80	559.90	133.40	252.20
1981--							
1st quarter	194.70	354.20	388.60	117.20	58.70	95.30	204.70
2d quarter							
3d quarter							
4th quarter							
1981 average							

Source--Forest Service, U.S. Department of Agriculture. Pacific Southwest Region is the State of California.

YEAR	ALLOWABLE CUT <sup>2</sup>	UNCUT VOLUME UNDER CONTRACT	RATIO
1970	1,151	2,041	1.8
1971	1,196	1,876	1.6
1972	1,249	1,665	1.3
1973	1,196	1,390	1.2
1974	1,196	1,503	1.3
1975	1,196	1,838	1.5
1976	1,196	2,077	1.7
1977	1,183	2,066	1.7
1978	1,183	2,204	1.9
1979	1,133	2,224	2.0
1980	1,134	2,484	2.2

Source--Bureau of Land Management.

<sup>1</sup>As of December 31 of each year.

<sup>2</sup>Includes an estimated 24 million board feet for eastern Oregon.

YEAR AND QUARTER	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME
	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft
1970	0	--	0	--	0	--	9	25,430	0	--	9	37,557	5	5,975
1971	0	--	0	--	0	--	8	20,285	0	--	21	64,198	1	7,170
1972	0	--	0	--	0	--	23	84,440	0	--	0	--	0	--
1973	0	--	0	--	2	25,600	12	18,740	0	--	0	--	0	--
1974	4	30,100	0	--	4	46,300	33	172,615	1	650	8	26,860	11	63,527
1975	4	13,855	0	--	5	66,920	18	147,050	2	2,135	8	56,320	17	66,390
1976	1	2,263	0	--	1	15,200	7	68,250	0	--	2	8,350	4	10,658
1977	3	13,800	7	63,290	8	69,000	13	192,500	0	--	10	70,450	15	76,379
1978	4	43,500	0	--	1	357	15	161,500	0	--	0	--	20	83,836
1979	5	42,760	4	2,150	11	79,460	0	--	0	--	19	11,575	34	86,586
1980	2	20,400	3	2,032	6	44,360	16	113,140	0	--	18	6,763	44	26,525
1981--														
1st qtr.	1	165	0	--	0	--	0	--	0	--	3	416	7	30,640
2d qtr.														
3d qtr.														
4th qtr.														

1981 total

YEAR AND QUARTER	OCHOCO		OKANOGAN		OLYMPIC		ROGUE RIVER		SISKIYOU		SIUSLAU		UMATILLA	
	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME
	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft
1970	0	--	3	18,700	7	26,675	0	--	0	--	0	--	2	22,000
1971	0	--	4	14,860	3	15,140	0	--	0	--	0	--	0	--
1972	0	--	0	--	8	32,897	0	--	0	--	8	26,356	11	198,116
1973	0	--	0	--	22	92,199	0	--	17	94,680	14	72,701	5	22,400
1974	0	--	3	19,000	12	78,990	28	98,752	12	52,775	34	174,471	11	74,710
1975	3	39,550	2	21,000	8	53,842	24	143,665	22	59,331	26	201,478	5	20,620
1976	3	19,270	2	9,300	5	45,579	18	46,254	7	22,335	17	118,763	6	23,110
1977	0	--	1	11,500	2	30,926	25	100,807	14	58,980	17	91,027	7	31,100
1978	5	34,300	0	--	6	44,615	47	171,251	13	62,300	39	231,303	0	--
1979	3	23,500	7	20,105	12	106,105	50	118,818	2	270	16	120,834	4	35,500
1980	1	7,700	2	10,600	12	69,100	31	123,125	7	29,510	7	45,137	3	18,200
1981--														
1st qtr.	0	--	0	--	0	--	16	31,020	0	--	20	98,274	1	6,500
2d qtr.														
3d qtr.														
4th qtr.														

1981 total

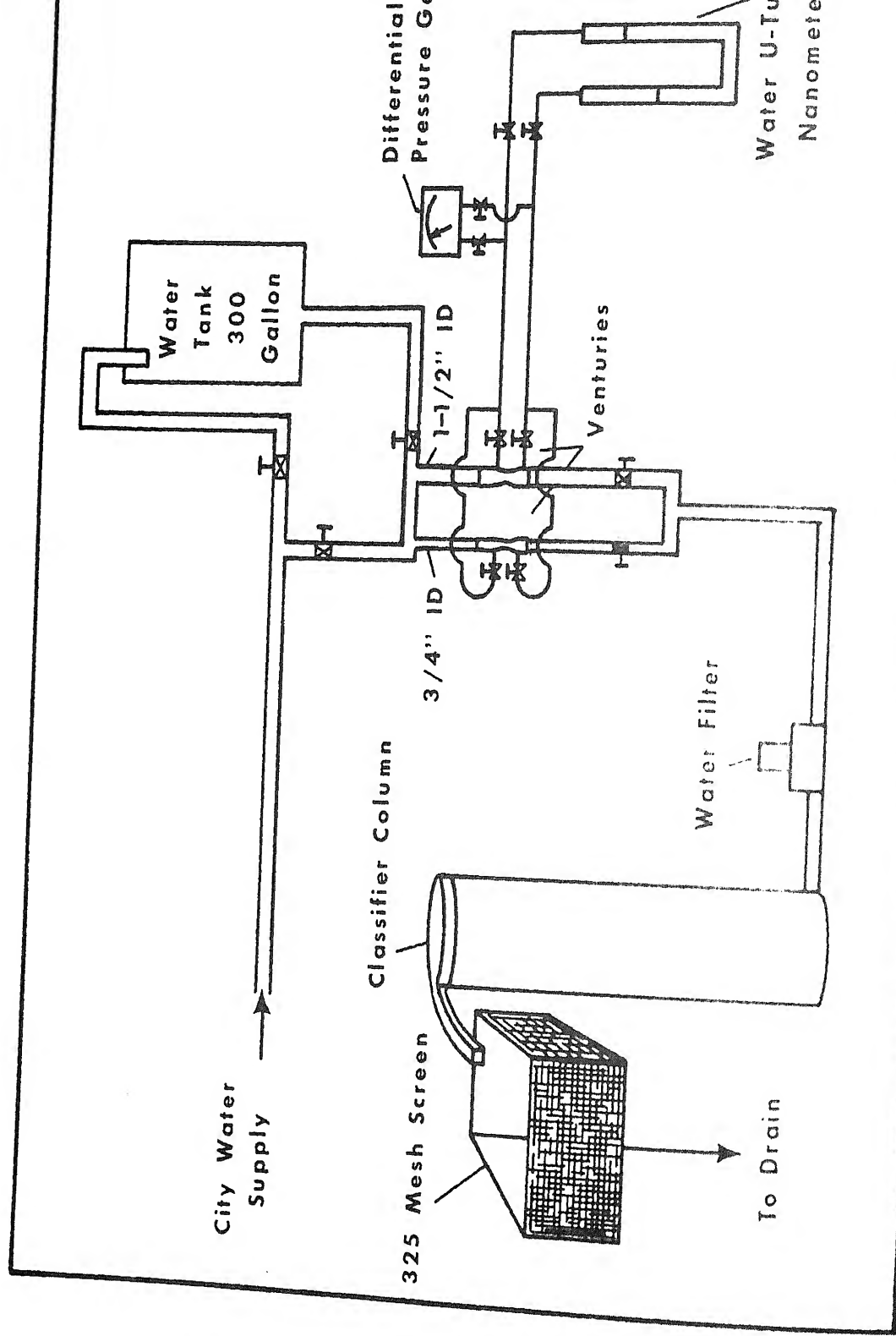
YEAR AND QUARTER	UMPQUA		WALLOWA-WHITMAN		WENATCHEE		WILLAMETTE		WINEMA		ALL FORESTS	
	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME	SALES	VOLUME
	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft	Number	Thousand bd ft
1970	2	7,316	0	--	3	3,386	0	--	0	--	40	147,039
1971	0	--	0	--	0	--	0	--	0	--	37	121,653
1972	0	--	0	--	0	--	0	--	0	--	50	341,809
1973	0	--	8	77,400	0	--	7	58,510	5	22,460	92	484,690
1974	22	124,807	0	--	0	--	7	61,520	5	35,550	195	1,060,627
1975	29	146,668	0	--	2	17,400	10	137,810	9	69,600	194	1,271,634
1976	21	55,093	0	--	0	--	19	121,100	5	38,040	118	603,565
1977	29	128,705	0	--	0	--	48	174,585	8	35,110	207	1,148,159
1978	29	125,330	0	--	0	--	33	177,660	13	60,006	225	1,195,958
1979	35	169,212	0	--	5	23,100	53	146,366	6	59,050	266	1,045,391
1980	31	166,650	7	1,799	4	18,000	83	197,229	4	30,400	281	930,670
1981--												
1st qtr.	30	91,385	1	135	1	500	6	2,036	5	50,450	91	311,521
2d qtr.												
3d qtr.												
4th qtr.												

1981 total

Source--Forest Service, U.S. Department of Agriculture. Pacific Northwest Region includes Oregon and Washington.

<sup>1</sup>July 1, 1974, Colville National Forest in Washington became part of the Pacific Northwest Region.

<sup>2</sup>July 1, 1974, Snoqualmie National Forest was merged with the Mount Baker National Forest.



flame technique. Arsenic, beryllium, chromium, copper, manganese, nickel, selenium, vanadium, zinc, antimony, sodium, and potassium. The cadmium and lead concentrations were too low in each of these coals to be detected by this flame technique; therefore, these elements were then determined by flameless graphite furnace technique utilizing apparatus specifically purchased for this determination. The apparatus will also be useful for low-concentration level determinations.

The solutions for flame and furnace atomic absorption as well as for atomic emission were prepared by dissolving the ash in teflon beakers with aqua regia/hydrofluoric acid (1:1) by boiling to dryness, adding nitric acid and diluting to volume.

Arsenic, selenium, and antimony were determined by a unique procedure developed at BCR based on Eschka fusion, hydride generation, and atomic absorption using a hydrogen-argon flame. This procedure is presently being considered for round-robin testing by ASTM Committee D05 on Coal and Coke.

Mercury was determined by a combustion bomb method developed at BCR by a double-gold amalgamation system constructed at BCR. Both techniques involve flameless atomic absorption and both are being considered for round-robin testing by ASTM Committee D05 on Coal and Coke. The first method has been tested with a great deal of success. Testing of the double-gold amalgamation system has been hampered by so few of the systems being available.

Fluorine was determined by a combustion bomb-selective ion electrode method. As the work progresses, the analytical techniques used, particularly for the trace-element determinations, including the most recent refinements are being written, tested, and modified where needed. Later they will be incorporated into an analytical procedures manual for submission with the final report for this sponsored program.

The results of analyses are displayed on data sheets developed to show the results of each analytical determination for each of the various fractions obtained during the cleaning. One example of these is shown as Figure 6 which contains the ash content for all of the fractions obtained during the cleaning of coal 1R, the first coal. From the data in this figure and the other similar data sheets, obvious analytical errors can be immediately spotted. In this case, they could be observed readily as interruptions in the trend of low to high ash content from clean coal to refuse fraction. With the voluminous data being obtained during the course of this project, it would be easy to miss such simple errors caused, perhaps, by an incorrectly recorded sample number. In one case in a previous study, each fraction obtained had a higher concentration value than the feed from which it came. This was traced to a dilution error during analysis. Displaying the data as in Figure 6 minimizes the chances for these kinds of errors.

The analytical results for the individual samples are displayed as shown in Figure 7. The individual samples were also divided into groups for a comparison.

ROM  
19.1

Coal: IR

[illegible]

Analytical Lab No: 77-1071Sample Code No: 1R-3M-2HCPROXIMATE, %

Moisture	<u>0.64</u>
Ash	<u>8.47</u>
Volatile Matter	<u>32.8</u>
Fixed Carbon	<u>58.7</u>

ULTIMATE, %

Carbon	<u>78.4</u>
Hydrogen	<u>5.20</u>
Nitrogen	<u>1.44</u>
Sulfur	<u>1.48</u>
Chlorine	<u>0.20</u>
Oxygen	<u>4.81</u>

SULFUR FORMS, %

Sulfate	<u>0.00</u>
Pyritic	<u>0.91</u>
Organic	<u>0.57</u>

MISCELLANEOUS

Calorific Value Btu/lb	<u>13,934</u>
---------------------------	---------------

MAJORS IN ASH, %

SiO <sub>2</sub>	<u>45.4</u>
Al <sub>2</sub> O <sub>3</sub>	<u>25.7</u>
Fe <sub>2</sub> O <sub>3</sub>	<u>16.0</u>
MgO	<u>0.86</u>
CaO	<u>5.82</u>
TiO <sub>2</sub>	<u>1.38</u>
MnO	<u></u>
Na <sub>2</sub> O	<u></u>
K <sub>2</sub> O	<u></u>
SO <sub>3</sub>	<u>1.52</u>
P <sub>2</sub> O <sub>5</sub>	<u>0.56</u>
	<u></u>
	<u></u>
	<u></u>

ELEMENT, ppm

Arsenic	<u>15.8</u>
Beryllium	<u>1.34</u>
Cadmium	<u>0.045</u>
Chromium	<u>16.3</u>
Copper	<u>13.7</u>
Fluorine	<u>65.9</u>
Lead	<u>6.64</u>
Manganese	<u>21.1</u>
Mercury (ppb)	<u>384</u>
Nickel	<u>14.1</u>
Selenium	<u>3.08</u>
Vanadium	<u>30.4</u>
Zinc	<u>19.9</u>
Antimony	<u>0.94</u>
	<u></u>
	<u></u>

Silicon	<u>18,200</u>
Aluminum	<u>11,700</u>
Iron	<u>9,620</u>
Magnesium	<u>450</u>
Calcium	<u>3,580</u>
Titanium	<u>711</u>
Manganese	<u></u>
Sodium	<u>135</u>
Potassium	<u>1,490</u>
	<u></u>
Phosphorus	<u>210</u>
	<u></u>
	<u></u>
	<u></u>

tion of the final report will describe the development in sufficient detail for use by coal industry and other agencies involved in similar work.

### Petrographic Methods

Petrographic analyses were employed to supplement the chemical analyses. The methods designed to characterize coal separates evolved from the gravity and sizing techniques. These analyses involve the use of a light microscope to identify and measure coal constituents and included impurities up to 100 microns in size. The following analyses were used to optically analyze each sample:

Coal composition: To identify and quantify the organic constituents characterizing the subject separate.

Pyrite mode of occurrence: To determine the relative association of the pyrite impurity with the coal. (Free, surface, or encased)

Pyrite size: To measure and quantify the mean projected area of the pyrite associated with the coal.

Results of the petrographic analyses will not be discussed in this brief paper.

### Data Evaluation

Further evaluation of the data was aided by use of a computer. Mass balances were calculated and concentrations of the products were calculated (a) based on the ultra-clean and clean coal fractions No. 1 and 2 on the ultra-clean and clean coal as well as the non-pyrite refuse fractions No. 1, 2, and 3; and (c) based on the middlings fractions No. 2. It might, in a real situation, be subjected to additional cleaning. The computer printout for the program written for the mass balance calculations is presented in Table 1. A differential value between the individual and composite is also calculated and displayed in order that judgment be made on the entire operation including the cleaning and analysis.

Most of these calculated values might not be needed to evaluate each coal and each group; however, they will be available and are easily accessible while the data are first being entered into the computer rather than to reenter all of the data at some later time. For one coal, the mass balances for 37 constituents and 18 different groups of feeds and products fractions could result in a total of almost 700 sets of individual calculations, such as that displayed in Table 1, available for evaluation.



Analysis:	Groups
1. <b>Demographics</b>	Age, Gender, Education, Income
2. <b>Attitudes</b>	Attitudes towards the environment, attitudes towards the company
3. <b>Behaviors</b>	Recycling, energy conservation, waste management
4. <b>Perceptions</b>	Perceptions of the company's environmental impact, perceptions of the company's commitment to sustainability
5. <b>Intentions</b>	Intentions to purchase sustainable products, intentions to support sustainable initiatives
6. <b>Engagement</b>	Engagement in sustainability initiatives, engagement in community activities
7. <b>Trust</b>	Trust in the company, trust in the government
8. <b>Knowledge</b>	Knowledge of environmental issues, knowledge of sustainable practices
9. <b>Values</b>	Values of sustainability, values of social responsibility
10. <b>Norms</b>	Norms of sustainability, norms of social responsibility

## ROM

**Coal:**

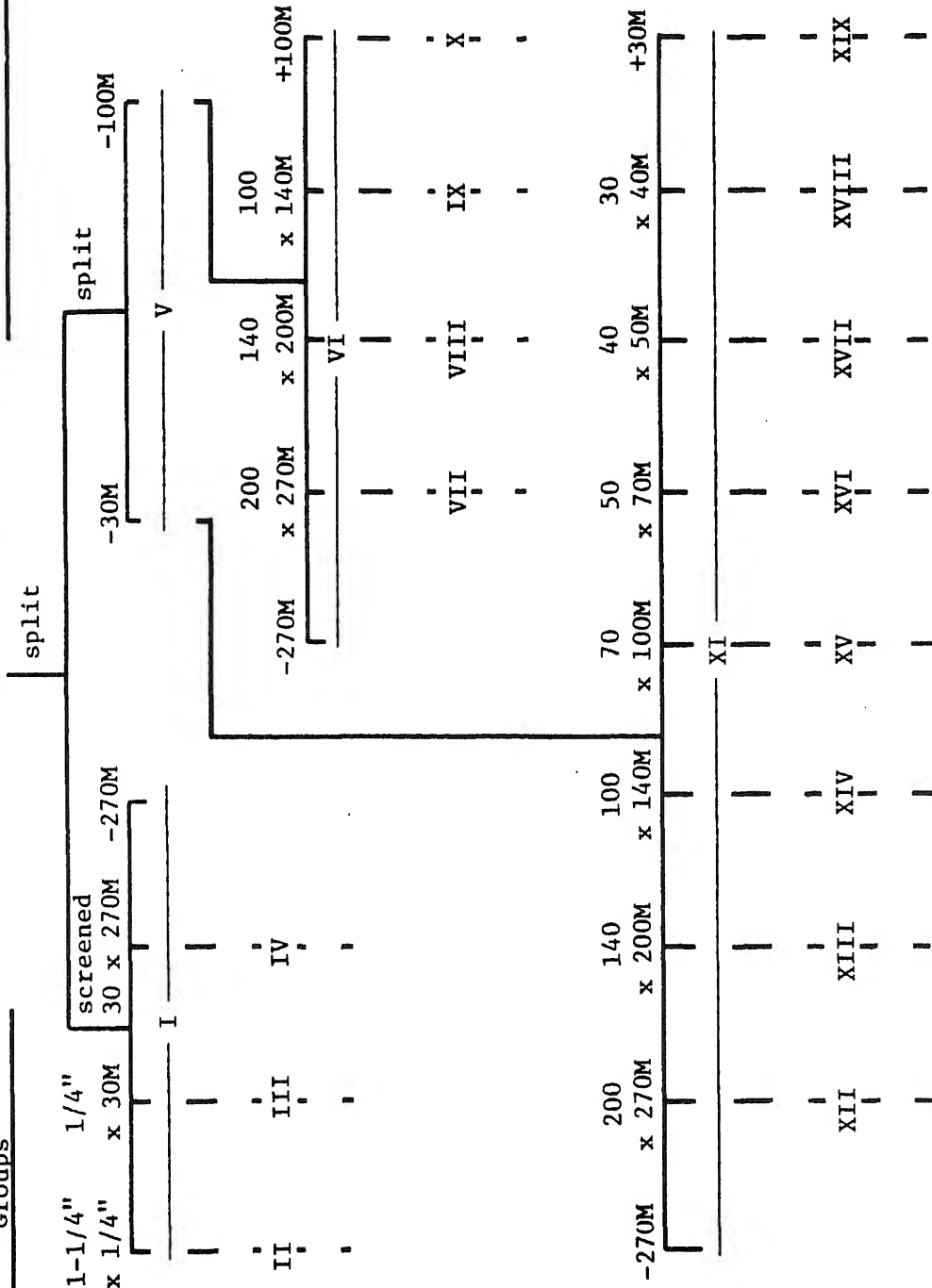


TABLE 1. SAMPLE PRINTOUT FROM MASS  
BALANCE CALCULATION PROGRAM

<u>FRACTION NUMBER</u>	<u>WEIGHT FRACTION</u>	<u>SULFUR CONCENTRATION</u>		<u>WEIGHTED CONCENTRATION</u>
1	0.574	1.09	=	0.626
2	0.155	1.76	=	0.273
3	0.055	3.80	=	0.209
4	<u>0.216</u>	3.58	=	<u>0.773</u>
	1.000			1.881
[C] IN FEED	= 1.76	(COMP.-FEED) DIFFERENTIAL =		
[C] IN CLEANED COAL	= 1.232	% REMOVED =		
*[C] IN CLEANED COAL	= 1.413	*% REMOVED =		
[C] IN MIDDLINGS	= 2.294	*% YIELD =		
[C] IN REFUSE	= 3.625	% YIELD =		

to demonstrate the relationships between the percent removed of each constituent with the percent removed of every other constituent. This was done as an additional means of comparing the effectiveness of the fugitive element removal of the two coals. At this time, the percent removed was selected as the parameter to be evaluated. Later, when data for more coals are available, relationships between concentrations will be examined more thoroughly.

## RESULTS AND DISCUSSION

Cleaning, analyses, and data evaluation of two coals are complete. One coal is a mixture of Upper and Lower Freeport seams and the other an Illinois No. 6 seam. Work on additional coals is in progress. The data were used in evaluating the effect of such cleaning on fugitive elements.

### Coal Sampling

A list of the twenty coal seams to be sampled is shown in Table 2. Fifteen of these have already been acquired and are available to the project.

### Coal Cleaning

The first three coals were extensively cleaned using both Procedure A and Procedure B; the fourth coal involved only the shorter Procedure A. For the weight percent, ash, total sulfur, and calorific value data for the first two coals, the cleaning strategies employed were particularly effective. The separations needed to attain the objectives of the project were being achieved.

Washability studies were utilized primarily to determine how much clean coal could be produced at a given specific gravity and to define the ash and sulfur characteristics of the coal at that gravity. A washability study was made by testing coal samples at carefully controlled specific gravities and analyzing the specific gravity fractions for ash and sulfur contents. A table was developed detailing the weight percentages and the ash and sulfur analysis for each fraction. The data were then mathematically combined to give "cumulative float" and "cumulative sink" for both ash and sulfur and were utilized to develop "washability curves" which helped to characterize the coal. One example of the washability tables developed for this study, one for the first coal, is presented in Table 3. The tables detail the separation gravities, the corresponding weight percentages, and the ash and sulfur analyses for each of the three size fractions.

The washability curves for the 31.8 x 6.35-mm (1-1/4 x 1/4-inch) fraction of coal 1R which was cleaned utilizing the heavy media unit are shown in Figure 9. Five curves are plotted on the chart: cumulative float ash (CFA), cumulative float sulfur (CFS), cumulative sink ash (CSA), cumulative sink sulfur (CSS), and the yield curve. As stated previously, these curves can be used to determine how much coal may be produced at a given specific gravity.

TABLE 2. COALS TO BE USED IN BCR FUGITIVE ELEMENT STUDY

<u>Sample</u>	<u>Seam</u>	<u>Sample</u>	<u>Seam</u>
1	Upper/Lower Freeport	11	Pocahontas No. 3
2	Illinois No. 6	12	Stockton
3	Rosebud	13	Sewell
4	Beulah-Zap	14	Mary Lee
5	Hannah No. 60	15	Kentucky No. 9
6	Adaville No. 1	16	Illinois No. 5
7	Castle Gate B	17	Imboden
8	Lower Kit- taning	18	Upper Elk- horn
9	Pittsburgh	19	Pittsburgh
10	Meigs Creek	20	Lower Kit- taning

TABLE 3. WASHABILITY ANALYSIS OF COAL 1R

<u>Specific Gravity</u>		<u>Separates, percent</u>			<u>Cumulative Recovery, percent</u>			<u>Cumulative Rejects, percent</u>		
<u>Sink</u>	<u>Float</u>	<u>Yield</u>	<u>Ash</u>	<u>Sulfur</u>	<u>Yield</u>	<u>Ash</u>	<u>Sulfur</u>	<u>Yield</u>	<u>Ash</u>	<u>Sulfur</u>
Group II 1-1/4 x 1/4 Inch Heavy Media - coarse										
	1.35	57.4	6.2	1.09	57.4	6.2	1.09	100.0	26.0	1.9
1.35	1.55	15.5	19.2	1.76	72.9	9.0	1.23	42.6	52.6	2.9
1.55	1.80	5.5	41.6	3.80	78.4	11.3	1.41	27.1	71.7	3.6
1.80		21.6	79.4	3.58	100.0	26.0	1.90	21.6	79.4	3.6
Group III 1/4 Inch x 30 Mesh Heavy Media - fine										
	1.35	79.6	5.9	1.06	79.6	5.9	1.06	100.0	15.7	2.2
1.35	1.55	6.8	22.8	2.64	86.4	7.2	1.19	20.4	54.2	6.8
1.55	1.80	5.2	55.8	5.67	91.6	10.0	1.44	13.6	69.9	8.9
1.80		8.4	78.6	11.0	100.0	15.7	2.24	8.4	78.6	11.0
Group IV 30 x 270 Mesh Hydraulic Classifier										
<u>Average</u>										
	1.27	31.9	6.6	1.06	31.9	6.6	1.06	100.0	12.9	2.2
	1.31	47.6	8.5	1.48	79.5	7.7	1.31	68.1	15.9	2.8
	1.42	14.9	19.4	2.90	94.4	9.6	1.56	20.5	33.0	6.0
	2.46	5.6	69.2	14.5	100.0	12.9	2.29	5.6	69.2	14.5

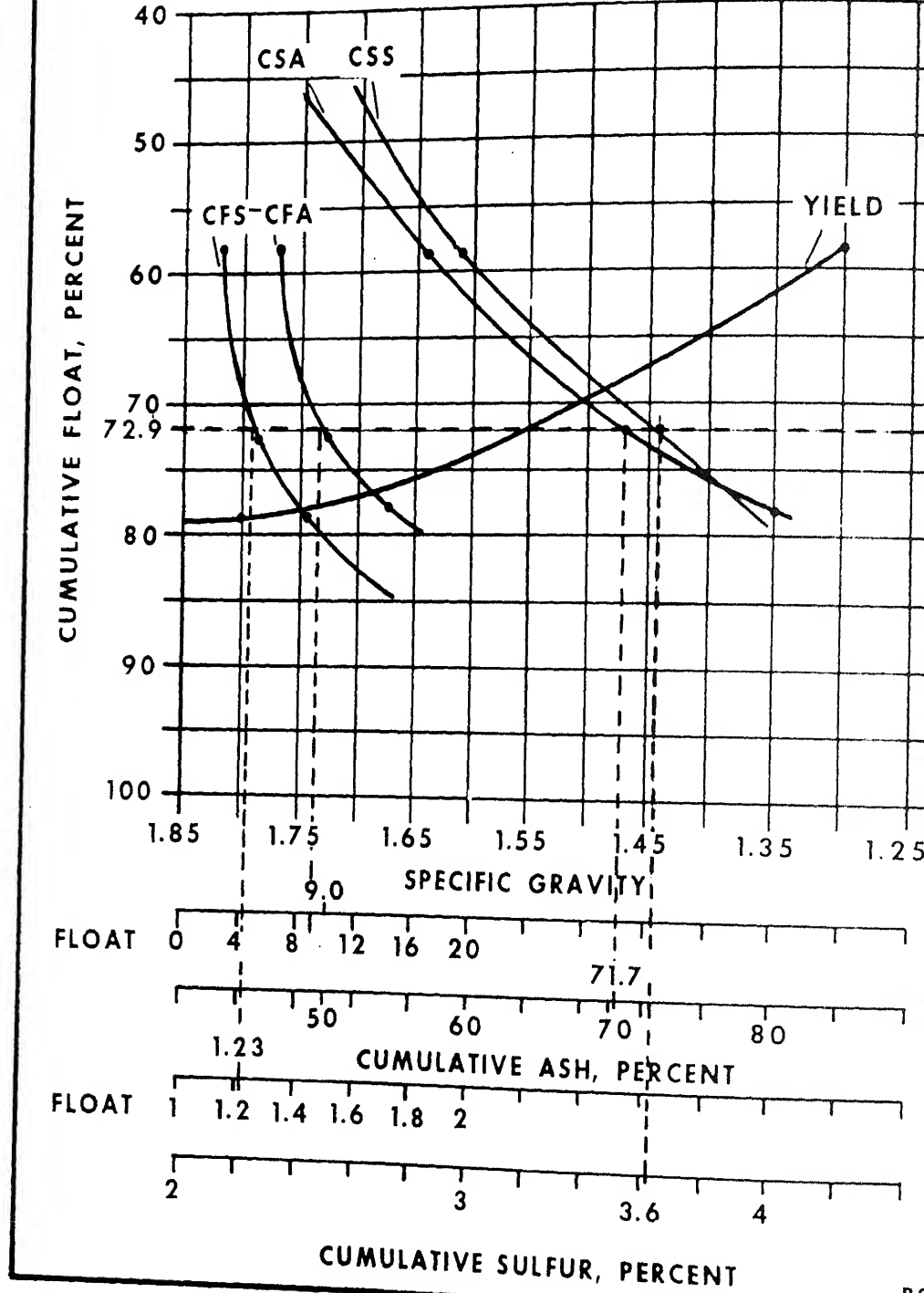


Figure 9. Washability Curves for the  $1\frac{1}{4} \times \frac{1}{4}$  In. Fractions of Coal 1R

By referring to Figure 9, it can be seen that if a 1.55 specific gravity were chosen for the cleaning gravity of the 31.8 x 6.35-mm (1-1/4 x 1/4-inch) fraction of coal 1R, the following results would be expected: the yield in the float fraction would be 72.9 percent of the total feed coal, the float fraction would contain 9 percent ash and 1.23 percent sulfur, the sink fraction would contain 71.7 percent ash and 3.6 percent sulfur. It should also be noted that the slope of the cumulative float curves gives a quick estimate of the difficulty of cleaning a coal. The greater the slope, the more near-gravity material and the more difficult the coal is to clean.

By interpreting the data presented and by utilizing the washability curves, general statements can be made about the characteristics of the coals and the response of the coals to cleaning.

For example, it can be inferred that coal 2R is more resistant to pulverization than 1R. Coal 2R contains a higher percentage of material in the coarse size fraction, 31.8 x 6.35-mm (1-1/4 x 1/4-inch), and a lower percentage in the fines, 30 x 270-mesh, than coal 1R. The higher percentage in the coarse screen fraction of coal 2R indicates that less degradation occurred during the screening, implying that coal 2R is harder than 1R.

When compared at a 1.45 specific gravity, the 6.35-mm (1/4-inch) x 30-mesh fraction showed the best ash reduction potential for both coals. The 31.8 x 6.35-mm (1-1/4 x 1/4-inch) fraction of coal 1R had the highest percentage ash reduction (72 percent), but the feed ash was much higher than in the 6.35-mm (1/4-inch) x 30-mesh fraction, which yielded a higher float ash even with the 72 percent reduction. The ash reduction potential at the 1.45 gravity was poor for both coals at the 30 x 270-mesh size range. From the washability curves, a lower specific gravity separation for the 30 x 270-mesh fractions would yield a better cleaning response.

Coal 1R showed better total sulfur reduction potentials than 2R for all size ranges at the 1.45 specific gravity. Coal 1R inherently has a lower sulfur content at the run-of-mine level and also proved, even for the 30 x 270-mesh fraction, to be easier to clean to an acceptable sulfur level.

The changes in the Btu levels between the raw coals and the coals washed at 1.45 gravity were not significant. Only the 31.8 x 6.35-mm (1-1/4 x 1/4-inch) fraction of coal 1R showed a reasonable increase, 22.9 percent. The fine fractions, 30 x 270-mesh, of both coals showed a large reduction in Btu's when cleaned at 1.45 gravity. Again, a specific gravity lower than 1.45 would show a better response for the fines of both coals.

the four are apparent. For coal 1R, it is 27 ppm; for coal 2R, it is 22 ppm; for coal 3R, it is 15 ppm. For the lignite, coal 4R, the average for the same 14 elements is only 8 ppm.

Thirty-eight constituents of samples of each of the first 20 coals, including the run-of-mine sample, were determined. Contamination was a continuing problem throughout the study. Instances of contamination with chromium, copper, lead, nickel, and zinc were identified and documented. These will be described thoroughly both in a forthcoming report and in a report on analytical procedures. Contamination was minimized by routinely analyzing reagent blanks and other material used in the project such as the magnetite used in the heavy media separation.

Every determination was done in duplicate. Lack of duplicate agreement immediately precipitated an additional determination. Whenever time allowed, more than one procedure was used for the trace element determinations as a check on the accuracy of the analytical values.

Finally, as a continual check on the analytical procedures used in this project, National Bureau of Standards (NBS) certified reference materials SRM-1632 Coal and SRM-1633 Fly Ash, were analyzed along with each run-of-mine coal and its cleaned fractions. One example of the type of agreement normally obtained between the determined values and the NBS values is presented in Table 5.

A more thorough description of the analytical procedures and the precision and accuracy studies is programmed at the end of the unfunded portion of this program, when the twenty coals have been analyzed and the effect of the cleaning on fugitive elements has been determined.

#### Mass Balance Calculations

The analytical data for each coal were used in calculating the mass balance for the various individual cleaning schemes for each coal. The mass balance for each of the determined constituents were calculated: (a) to check the integrity of the cleaned fractions and the validity of the analytical data by comparing the summation of the materials in each fraction with the total material, and (b) to evaluate the reduction or enrichment of each element as a result of the cleaning process.

For each constituent, the concentration determined in a particular fraction was multiplied by the weight fraction of the feed material reported to that zone. The weighted concentrations thus obtained



TABLE 4. COMPARISON OF CONCENTRATIONS OF RUN-OF-MINE  
COALS 1R, 2R, 3R, AND 4R (dry coal basis)

	<u>Coal 1R</u>	<u>Coal 2R</u>	<u>Coal 3R</u>	<u>Coal</u>
Ash, percent	22.3	16.0	15.8	11
Total Sulfur, percent	2.30	2.73	1.18	0.8
Chlorine, percent	0.12	0.33	0.01	0.0
Pyritic Sulfur, percent	1.78	2.01	1.02	0.7
Organic Sulfur, percent	0.46	0.50	0.14	0.1
Arsenic, ppm	40.2	11.0	8.54	10.
Beryllium, ppm	1.84	1.10	0.87	0.7
Cadmium, ppm	0.08	0.47	0.12	0.0
Chromium, ppm	29.7	21.1	8.21	5.1
Copper, ppm	22.1	11.0	13.2	6.9
Fluorine, ppm	115	113	63.6	32.
Lead, ppm	15.4	21.8	12.8	1.8
Manganese, ppm	50.0	36.8	65.2	33.
Mercury, ppb	662	154	154	11
Nickel, ppm	20.9	18.4	4.98	4.6
Selenium, ppm	6.20	1.83	1.61	0.9
Vanadium, ppm	44.4	26.2	14.0	10.
Zinc, ppm	35.5	91.8	12.8	3.4
Antimony, ppm	1.09	0.40	1.78	0.5
Sodium, ppm	448	1,230	248	6,63
Potassium, ppm	5,460	2,980	1,110	57
Silicon, ppm	57,800	37,900	39,800	14,50
Aluminum, ppm	30,800	17,700	20,200	6,47
Iron, ppm	21,100	19,100	8,560	7,84
Magnesium, ppm	1,360	870	3,150	4,06
Calcium, ppm	2,090	3,110	6,790	16,10
Titanium, ppm	1,670	1,010	1,090	37
Phosphorus, ppm	260	160	85	14
Calorific Value, Btu/lb	11,640	11,902	10,990	10,55

TABLE 5. COMPARISON OF TRACE ELEMENT CONCENTRATIONS  
IN SRM-1632 COAL WITH NBS CERTIFIED VALUES  
(All values in ppm on a dry coal basis)

<u>Element</u>	<u>Average ppm Determined</u>	<u>NBS Value, ppm</u>
Antimony	3.47*	not certified
Arsenic	6.22	5.9 ± 0.6
Beryllium	1.63	1.5 <sup>†</sup>
Cadmium	0.17	0.19 ± 0.03
Chromium	20.5	20.2 ± 0.5
Copper	17.7	18 ± 2
Lead	31.7	30 ± 9
Manganese	45.6	40 ± 3
Nickel	14.1	15 ± 1
Potassium	2,680*	not certified
Selenium	2.88	2.9 ± 0.3
Sodium	362*	not certified
Vanadium	36.4	35 ± 3
Zinc	41.6	37 ± 4

\* In agreement with other published values.

† Informational value.

the concentration in the refuse.

The differential between composite and feed was obtained from each mass balance calculation as follows:

$$\text{Differential} = \frac{\text{Composite Value} - \text{Feed Value}}{\text{Feed Value}} \times 100$$

These values, since they indicate the extent of agreement between feed and product constituents, can offer much insight into both the cleaning and the analytical study. Judgments are possible on the cleaning process based on the agreement of many of the constituents within any one cleaning operation. Poor agreement generally might indicate problems with the integrity of the samples obtained by cleaning; good agreement with the exception of one or two constituents, might indicate problems in the analytical determination of the constituents. A consistent positive or negative bias would indicate gain or loss of a constituent during cleaning or analysis, or analytical problems with certain of the fractions, perhaps the clean coal or (more likely) the refuse.

The average percent differentials for each of the first four coals are summarized in Table 6. The values presented in the table are the average (absolute value) from as many as 18 values from the individual cleaning operations. Low values indicate good agreement between composite and feed. Obviously, there is a great deal of satisfaction with these values. For the most part, the agreement was better for coals 1R, 2R, and 3R than it was for coal 4R.

Some of the lack of agreement can be attributed to the low concentrations of trace constituents associated with this fourth coal. The concentrations in solution were often at or near the detection limits of the analytical methods. Additionally, slight contamination of trace constituents routinely experienced and tolerated in previous analyses exerted a greater influence on results at the low concentration levels. Such low concentration levels will probably be experienced with other coals for this project.

#### Effect of Cleaning on Distribution and Removal

The analytical data were used in evaluating the effect of cleaning on run-of-mine coals on fugitive element removal. An example of the type of data available, a summary of the percent of each constituent removed as a result of cleaning coal 1R, is presented in Table 7.

This calculation assumes the first two fractions as the cleaned coal and the last two as the refuse. The corresponding product recovery for each group is presented at the top of each column in this table. Most of the constituents which were concentrated, not removed, by the cleaning were not included in this table. For the most part, these were inherent parts of the

AVERAGE PERCENT DIFFERENTIAL  
COALS 1R, 2R, 3R, and 4R

	<u>Coal 1R</u>	<u>Coal 2R</u>	<u>Coal 3R</u>
Ash	2	3	5
Volatile Matter	2	1	1
Fixed Carbon	1	1	1
Carbon	1	1	1
Hydrogen	2	3	3
Nitrogen	2	2	5
Total Sulfur	4	2	5
Chlorine	11	6	19
Pyritic Sulfur	5	3	7
Organic Sulfur	5	3	11
Calorific Value	1	1	1
Arsenic	15	8	11
Beryllium	4	3	5
Cadmium	14	21	9
Chromium	3	8	7
Copper	14	17	8
Fluorine	9	7	6
Lead	14	14	9
Manganese	3	7	4
Mercury	13	61	18
Nickel	9	8	25
Selenium	6	15	7
Vanadium	5	5	3
Zinc	6	21	23
Antimony	8	12	11
Sodium	10	11	10
Potassium	8	4	4
Silicon	4	4	4
Aluminum	4	4	3
Iron	5	5	9
Magnesium	7	4	11
Calcium	7	7	12
Titanium	3	4	5
Phosphorus	6	11	4
Average	6	9	8

Constituent	GROUP															
	II	III	IV	XII	XIII	XIV	XV	XVI	XVII	XVIII	XIX	VII	VIII	IX	X	Av.
	Product Recovery, percent															
	<u>73</u>	<u>86</u>	<u>80</u>	<u>71</u>	<u>76</u>	<u>79</u>	<u>80</u>	<u>83</u>	<u>81</u>	<u>76</u>	<u>69</u>	<u>82</u>	<u>82</u>	<u>75</u>	<u>63</u>	<u>77</u>
Ash	75	60	52	73	69	67	70	66	70	73	71	52	55	71	81	67
S <sub>T</sub>	52	54	54	78	71	65	66	60	62	66	76	68	63	72	82	66
Cl	8	4	15	14	11	11	7	5	6	8	8	8	7	10	13	9
S <sub>pyr</sub>	65	69	66	89	83	79	82	78	80	81	86	80	78	85	91	79
S <sub>org</sub>	10	6	15	18	14	13	12	7	8	8	10	11	10	13	26	12
As	82	79	71	92	88	88	91	86	89	88	93	87	86	93	97	87
Be	45	22	26	38	37	28	29	26	29	38	44	23	25	37	50	33
Cd	63	53	52	64	68	63	66	63	78	67	69	58	56	66	78	64
Cr	64	41	34	51	48	45	50	46	51	56	60	35	39	55	65	49
Cu	61	50	48	66	63	57	61	55	58	64	64	49	48	64	76	59
F	61	42	42	55	56	53	56	43	51	55	61	30	31	49	67	50
Pb	71	62	59	71	70	72	73	73	75	81	65	60	66	82	88	71
Mn	89	77	58	85	83	82	85	81	85	87	82	69	75	87	93	81
Hg	55	67	69	73	72	71	65	71	70	76	82	68	64	59	92	70
Ni	53	42	42	60	58	64	55	45	50	61	64	46	49	60	72	55
Se	44	65	67	82	78	73	75	74	72	79	83	74	72	80	88	74
V	63	36	31	47	39	41	42	39	44	55	58	30	32	52	66	45
Zn	74	58	45	71	66	61	66	62	65	71	65	51	51	67	78	63
Sb	29	33	28	36	42	30	35	22	32	28	52	28	29	41	60	35
Na	73	46	45	66	61	56	61	56	61	65	64	42	46	62	73	58
K	80	67	55	73	69	53	72	69	74	78	72	49	54	73	83	68
Si	77	61	51	72	68	67	69	68	71	74	71	49	54	71	80	67
Al	69	52	46	65	60	59	61	58	62	68	64	42	47	63	73	59
Fe	73	72	67	91	85	84	86	83	84	87	87	82	78	90	94	83
Mg	85	67	52	72	69	70	73	72	77	84	75	48	55	74	84	70
Ca	53	42	38	77	76	69	67	58	58	59	62	59	59	68	76	61
Ti	68	49	42	59	56	52	55	52	58	64	62	43	42	60	71	56
P	46	24	34	51	44	38	43	37	31	43	53	33	35	45	61	41
Average	60	50	47	63	61	58	60	56	59	63	64	49	50	62	74	58

\*Cleaned Coal = Fractions 1 and 2

amounts in the feed.

The averages by group and by constituent reflect generally good results for most of the constituents. Arsenic, iron, manganese, pyritic sulfur, and nickel were removed most effectively. Antimony, phosphorus, and vanadium were removed least effectively. Lead, mercury, and magnesium were actually concentrated slightly in the clean coal.

Similar data are available for each coal, assuming either the first or first three fractions from the heavy media or the hydraulic classification separations as the cleaned coal. The data are further summarized, by constituent for the first four coals. The values presented in Table 7 are the averages from the individual values for each of the cleaning fractions, for example, from the last column on the right in Table 7.

The differences in the effectiveness of cleaning each coal can be seen from the data in Table 8. Most constituents were removed more effectively from coal 1R than from the other coals, but the product was also the lowest for this coal. Cleaning was least effective with coal 4R, the lignite. However, the principal reason for this is simply the concentrations of the impurities in this coal, as previously displayed in Table 4, were relatively low prior to cleaning.

It must be pointed out at the same time that the calorific value of coal was also the lowest of the four. Perhaps the concept of a coefficient of expression relating the concentration of impurities per calorific value, similar to the "pounds of sulfur per million Btu's," is needed to compare and trace impurities in a wide variety of coals on an equal basis.

Differences in the relative rates of removal for each coal can be observed from the data in Table 8. Cadmium and zinc were removed more effectively from coal 2R than from the others. They were also present in higher concentrations in this coal from the Illinois basin than in the other coals.

Linear correlation coefficients and F-test ratios were calculated for each of the constituents to demonstrate the relationships between the percent removed of each constituent with the percent removed of every other constituent. These relationships were evaluated among "percent" of the constituents removed rather than among "concentration" of each constituent removed. This was done simply because two coals are not a statistically significant representation to permit drawing any specific conclusions concerning the general and the effect of cleaning them on fugitive element removal. Further concentration data will prove more meaningful later in the study when more coals are cleaned.

## FOR ALL GROUPS

	<u>Coal 1R</u>	<u>Coal 2R</u>	<u>Coal 3R</u>	<u>Coal 4R</u>
Product Recovery	77	87	87	87
Btu Recovery	91	97	92	92
Ash	67	48	41	41
Total Sulfur	66	46	56	56
Chlorine	9	8	16	16
Pyritic Sulfur	79	55	61	61
Organic Sulfur	12	9	16	16
Arsenic	87	53	70	70
Beryllium	33	20	21	21
Cadmium	64	77	34	34
Chromium	49	28	29	29
Copper	59	37	28	28
Fluorine	50	33	26	26
Lead	71	61	31	31
Manganese	81	65	20	20
Mercury	70	42	41	41
Nickel	55	25	27	27
Selenium	74	34	45	45
Vanadium	45	23	25	25
Zinc	63	71	30	30
Antimony	35	19	22	22
Sodium	58	25	28	28
Potassium	68	39	53	53
Silicon	67	43	43	43
Aluminum	59	42	37	37
Iron	83	65	76	76
Magnesium	70	42	13	13
Calcium	61	72	14	14
Titanium	56	34	33	33
Phosphorus	41	66	21	21
Average	58	42	34	34

The F-statistic was then utilized in evaluating the relations at the selected confidence level. The relationships are summarized in Table 9 for the first two coals. Only those having the highest degree of correlation are listed. Even with the imperfect means of evaluation, the two coals, particularly in the case of the first coal, show a high degree of correlation.

These studies with the first few coals, as well as previous cleaning studies at BCR with eight coals have confirmed that removal of potentially harmful trace elements can be effected by coal cleaning studies thus far with the coals reported here revealed differing results to the various cleaning processes. Generalizations concerning the cleaning of fugitive elements are not possible at this time. Speculations concerning elemental distributions are not possible either. Some trends have already been noted and these will be reexamined. A statistically significant number of coals have been cleaned and analyzed. Studies with additional coals are planned and already under way.

The program is flexibly designed to add or delete constituents by mutual agreement between the sponsor and BCR, as a result of new legislation, or by some new evidence of environmental contamination. An extensive cleaning scheme will also be similarly modified when warranted by the initial results of the studies. Milestones in reporting for the program include a report in preparation on the state-of-the-art of fugitive emissions as they relate to the coal industry, as well as two final reports: one describing the results of the studies, the other including a detailed description of the analytical procedures used in the study.

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ST	Si, Al, Mg, Ti	Spyr, Fe
Cl	Spyr	Sorg
Spyr	ST, As	ST, Pb, Fe
Sorg		P.R.*, Cl
As	Spyr, Fe	
Be	P.R.*, Cr, V, Na, Ti, P	V, Ti
Cd		Zn
Cr	Ash, Be, V, Zn, Na, Si, Al, Mg, Ti	V
Cu	Ash, Zn, Na, Al, Ti	
F	Ash, Na, Al, Ti	K, Si, Mg
Pb		Spyr, Fe
Mn	Ash, Zn, Si, Al	Ca
Hg		
Ni		
Se		
V	Be, Cr, Na, Al, Ti	Be, Cr, Ti
Zn	Ash, Cr, Cu, Mn, Na, K, Si, Al, Mg, Ti	Cd
Sb		
Na	Ash, Be, Cr, Cu, F, V, Zn, Si, Al, Mg, Ti	
K	Zn, Si, Al, Mg, Ti	Ash, Si, Mg, P
Si	Ash, Cr, Mn, Zn, Na, K, Al, Mg, Ti	Ash, F, K, Al, Mg
Al	Ash, Cr, Cu, F, Mn, V, Zn, Na, K, Si, Mg, Ti	Ash, Si
Fe	Spyr, As	ST, Spyrr, Pb
Mg	Ash, Cr, Mn, Zn, Na, K Si, Al, Ti	Ash, F, K, Si
Ca		Mn
Ti	Ash, Be, Cr, Cu, F, V, Zn, Na, K, Si, Al, Mg	Be, V
P	P.R.*, Be	K

\*P.R. = Product Recovery

## ABSTRACT

The aqueous drainage from coal piles and coal refuse dumps frequently is contaminated with acids and a variety of trace elements and inorganic compounds. The Los Alamos Scientific Laboratory is conducting research, jointly with DOE/ECT and EPA, to assess the nature and magnitude of trace element contamination in the drainage from coals and coal preparation wastes, to identify the elements of environmental concern in these effluents, and to define needed environmental control technology for this form of environmental pollution. The emphasis of this program is on the laboratory assessment of environmental control options for the drainages from high sulfur coals and coal preparation wastes. This presentation will review some of the accomplishments of this research to date, and discuss the various drainage control options available to the coal industry.

## INTRODUCTION

It has been well established that the drainage from coal refuse dumps is highly contaminated with trace or inorganic elements; however, little is known about the quantities of undesirable elements that are released into the environment from this source.<sup>(1)</sup> Development of the necessary control technology for human and environmental protection requires quantitative evaluation of the extent and severity of the problem. LASL has been directed by DOE/ECT to assess the nature and magnitude of the trace elements in the drainage from coal preparation wastes, to identify the trace elements of greatest environmental concern in these materials, and to evaluate required pollution control technology for this form of environmental contamination.

The research in this program is being conducted in several phases. The first phase included studies of the structure and weathering and leachability of the trace elements in selected samples of high sulfur refuse. These investigations established the overall potential of these materials to cause trace element contamination, and revealed the identities of the trace elements of concern in the refuse and coal pile effluents. The information gathered on refuse and coal structure and environmental behavior provides the basis for the present phase of the program, which involves the development of control technology to lessen the environmental impact of trace element pollution of coal or refuse associated waters.

Research has now been started to identify suitable means to control trace element contamination of the drainages from high sulfur coal preparation wastes. These control techniques can be roughly divided into three categories: immobilization or removal of contaminants prior to disposal of

## EXPERIMENTAL

The coal preparation wastes used in this work were collected from three coal cleaning plants (designated Plants A, B and C) in the Illinois Basin. These samples of high sulfur coal refuse are typical of the wastes produced by cleaning of the major coal types currently mined in the region.<sup>(2)</sup>

Both static and dynamic leaching experiments were conducted to evaluate the behavior of the trace elements in the Illinois Basin coal wastes under simulated environmental conditions and to test the effectiveness of potential environmental control methods. The static experiments were carried out by agitating a known quantity of crushed refuse or composite (50 g) in the presence of a constant volume of distilled water (200 ml) for varying periods of time. In the dynamic or column leaching tests, a crushed sample (~ 1500 g) was packed into a 70-cm-long by 4.6-cm-diam glass column and distilled water was continuously monitored through the column at a rate of 0.5 ml/min. The elemental compositions of the experimental leachates were determined by neutron activation analyses, atomic absorption spectrophotometry, optical emission spectroscopy and wet chemical methods.<sup>(2,3)</sup>

## RESULTS AND DISCUSSION

Static and dynamic leaching experiments were performed to evaluate the trace element behavior of Illinois Basin coal wastes under simulated weathering conditions. These experiments were done to provide information needed to predict quantitatively the trace element levels in the drainage from coal refuse dumps or disposal areas and to identify those elements of environmental concern.

Perhaps the single most important characteristic of the high sulfur refuse materials during aqueous leaching is their pronounced tendency to rapidly produce acidic leachates. This is due to the oxidative degradation of the pyrite and marcasite present in the refuse. Acid formation is partially attenuated by calcite or other neutralizing species in the refuse, but the leachates from Illinois Basin refuse samples that we studied nearly always had pH values in the range of 2 to 4. These acid leachates are very efficient at dissolving or degrading many of the mineral components of the refuse, and thus releasing the trace or minor elements associated with them.

Two types of trace element leachabilities were observed for all of the Illinois Basin refuse samples. Because of their abundances in the refuse some elements (such as Fe, Al, Ca, Mg) are released in relatively high absolute quantities. Other, less abundant elements (for example, Ni, Co, Zn, Cu) are leached in a high proportion to the total of each present, although this may not be a large amount in the absolute sense. The first group is highly concentrated in the leachates, the second is highly leachable from the refuse.

provides a means for directly determining which of the contaminants in the water solutions, such as those of interest here, exceed concentrations safely assimilated by the environment. Application of the MEG method to the composition of refuse leachates obtained in this work, and information in the literature, has revealed that nine elements, Ni, Zn, As and Cd are frequently present in potentially hazardous waste. Although these elements are not necessarily the only ones in the refuse that could conceivably be troublesome under all circumstances, they are the priority elements that are receiving the greatest emphasis in current work on environmental control technology.

Two basic approaches to effect trace element controls are being investigated in this work. The first involves methods to treat newly produced refuse either at the preparation plant or during disposal to prevent the release of trace elements from the disposal site. These techniques include refuse calcining, treatment of the refuse to remove acid forming components, labile trace elements, and the application of adsorbents or attenuation to refuse disposal sites. The second approach concerns techniques to abate the trace-element composition of already contaminated water flowing from refuse dumps or disposal areas. Under consideration here are methods such as alkaline neutralization, ion exchange, reverse osmosis, chelation and fixation of selected adsorbents.

One of the more promising techniques under consideration to immobilize hazardous elements in high sulfur coal refuse materials is calcining the refuse to high temperatures to produce an inert glass-like slag. Research in this area is directed both at identifying the chemical and physical changes brought about in the refuse structure as a result of the heat treatment and defining the consequent decreases in trace element mobility.

An initial set of calcining experiments was performed using high sulfur preparation wastes from Plant B (Illinois Basin). The sample was crushed to -3/8 in. and calcined in a quartz tube at 850°C in air for 6 h. The calcined material, which had partially fused, was reground to -20 mesh for subsequent studies. The analysis of the composition of the calcined refuse sample showed that most of the trace elements remained in the calcined sample (Table I). A decrease in the concentration of just a few volatile components in the refuse was noted. Of particular interest was the loss of sulfur that occurred as a result of the calcining process. The original concentration of 13.4% S by weight in the non-calcined sample described sample treatment yielded a product that contained only 1.2% S by weight. From the standpoint of removal of the acid-forming components from coal refuse, these results are quite remarkable since they show that calcining in air at 800-850°C is a method that can substantially reduce the potential in the coal refuse wastes. Other volatile components whose concentrations were decreased by the calcining were Br, Pb, and Cd.

THE EFFECT OF CALCINING AT 800°C ON THE  
TRACE ELEMENT COMPOSITION OF AN ILLINOIS BASIN  
COAL REFUSE SAMPLE

<u>Element<sup>a</sup></u>	<u>Uncalcined Refuse</u>	<u>Calcin Refus</u>
Al (%)	5.9	11.5
Mn	144	191
Fe (%)	11.0	19.0
Co	30	70
Ni	71	110
Cu	35	73
Zn	149	296
Cd (ppb)	400	290
Pb	34	12
S (%)	13.4	1.1

<sup>a</sup>Elemental compositions reported as ppm unless otherwise indicated.

Another set of calcining and leaching experiments was performed to determine optimum heat treatment conditions necessary to chemically immobilize the potentially toxic trace elements in the refuse matrix. These experiments were performed using high sulfur coal preparation wastes from Plants B and C (Illinois Basin). The wastes were ground to -20 mesh and calcined in air at 600°C, 800°C, 1000°C, and 1200°C for 2 h. The calcined residues were then statically leached (stirred with distilled H<sub>2</sub>O) for a period of 48 h using a ratio of 4 ml H<sub>2</sub>O to 1 g of calcined refuse, and pHs and total dissolved solids determined. The data are summarized in Table II. It is seen that heating to 600°C and higher results in a leachate with an elevated pH -- this is a consequence of the removal of the volatile, acid-forming sulfur component and is consistent with experimental data on sulfur volatilization. Calcining at 1000°C also results in a strong decrease in the leachate's total dissolved solids. Physically, samples calcined at 1000°C showed signs of sintering. It appears, based on

<u>Sample Source</u>	<u>Calcining Temp., °C</u>	<u>Sample Wt. Loss, %</u>	<u>Leachate pH</u>
Plant C	Uncalcined		2.9
Plant C	600	23	6.6
Plant C	800	23	6.2
Plant C	1000	23	7.8
Plant C	1200	23	8
Plant B	Uncalcined		1.8 <sup>b</sup>
Plant B	1000	38	7.0

<sup>a</sup>Static leaching of 20 g of crushed refuse with 100 ml of water.

<sup>b</sup>Leachate pH measured after 4.4 h of leaching.

illustrated by the data from a comparison leaching experiment on the refuse samples (Plant C) that had been calcined at 1000 °C. The calcined and uncalcined refuse samples listed in the table were subjected to static leaching for 48 h. It is seen from the information in the table that calcining has essentially eliminated the acid generation of the refuse samples and that the TDS contents of the resulting leachates are substantially reduced. More important is the fact that the concentrations of the abbreviated group of toxic elements listed have been reduced in the calcined refuse leachates by about two orders of magnitude over the values found in the leachates produced from the raw refuse materials.

Several methods are being considered to treat coal refuse during its disposal to prevent the release of trace contaminants during subsequent waste disposal or leaching by surface or ground water. These include coating the refuse material with neutralizing agents or trace element adsorbents, application of water tight sealants to all or parts of the waste.

Especially promising among these techniques is the codisposal of the refuse materials with alkaline agents such as lime. In one set of experiments, powdered lime in varying amounts (3 to 50 g) was slurried with distilled water with 3/8 in. high-sulfur coal refuse (530 g) from Basin Plant B. The

TRACE ELEMENT LEACHABILITY OF A PLANT C COAL REFUSE  
SAMPLE CALCINED AT 1000°C FOR 2 H.<sup>a</sup>

	<u>Uncalcined Refuse</u>	<u>Calcined Refuse</u>
pH <sup>b</sup>	2.9	7.
TDS (%)	.6	.
Al	100	<.
Fe	600	<.
Mn	5.8	.
Co	2.8	<.
Ni	4.7	<.
Zn	2.8	.

<sup>a</sup>Results from static leaching of 50 g of crushed refuse material with 200 ml of water for 48 h.

<sup>b</sup>Leachate compositions reported as ppm unless otherwise noted.

to -3/8 in. particles. Four different lime concentrations were employed: 1.5, 3 and 10 wt %. In addition, a control refuse sample that had not been lime-treated was also incorporated into this study for comparison purposes.

Column leaching experiments were conducted with about 500 g of each of the samples to determine the effects of the lime additions. The refuse mixtures were packed into pyrex columns 25 cm long by 5 cm diameter and subsequently leached with distilled water at a flow rate of 0.5 ml/min until more than 4 l of water had been passed through the refuse beds. The compositions of the leachates after about 300 ml of water had passed through the columns containing the refuse are given in Table IV.

Although the data are not listed in Table IV, the leaching experiments showed that the addition of 0.5 and 1.5 wt % lime to the acid refuse had only a small influence on leachate pH and trace element concentration because the acid neutralization provided by these amounts of lime was overwhelmed by the acid generating capability of the refuse. The additions of 3 and 10 wt % of the lime on the other hand (Table IV), did indeed effectively counteract the acid pro-

	Untreated Refuse Control	Refuse + 3% Lime	Re
pH <sup>b</sup>	2	7	
TDS (%)	4	0.4	
Al	720	<0.6	
Fe	7800	40	
Mn	22	1	
Co	12	0.3	
Ni	18	0.5	
Zn	29	0.1	

<sup>a</sup>Results from column leaching experiments with Illinois Basin PI (see text).

<sup>b</sup>Leachate compositions are reported as ppm unless otherwise noted.

The system containing 3 wt % lime is especially interesting because a pH of 7 was maintained for nearly the entire duration of the leaching (until 4.2 l had been passed through the column). TDS values for the lime combination were also very respectable (ranging downward from 4% to 0.1%) especially considering that the dissolution of the lime contributed substantially to the dissolved solids content of the solution.

Another potentially fruitful way to retain the leachable contaminants at a refuse disposal site is to intermix the acid coal wastes with suitable solid sorbent materials to evaluate their trace element attenuation prior to using these agents in codisposal experiments. An example of one of the solid sorbents in this area will illustrate the potential utility of the method.

In this experiment, acidic coal refuse leachates were equilibrated with various solid sorbent materials to evaluate their trace element attenuation prior to using these agents in codisposal experiments. The solid sorbents used were illite, montmorillonite, and kaolinite clays; a sample of scrubber precipitator ash and two samples of bottom ash, each from different sources; and an acid drainage treatment sludge; and a clay-rich soil. The



leachate pH elevation, and attenuation of 13 trace elements that have been identified as being of greatest environmental concern in the Illinois Basin refuse effluents. The data have been isolated into different sections in VI to draw attention to some of the pertinent features. For example, since solubilities of  $\text{Fe}^{+3}$  and  $\text{Al}^{+3}$  are very sensitive to pH in acidic solutions sorbents that are most effective in elevating the pH above a value of 5 are most effective in decreasing the concentrations of Fe and Al. In Table VI the pH, Fe, and Al results are grouped together it is seen that 7 of the 1 sorbents tested are very effective.

TABLE V  
THE ATTENUATION OF TRACE ELEMENTS IN COAL REFUSE  
LEACHATES BY VARIOUS ATTENUATING AGENTS<sup>a</sup>

	<u>Untreated Leachate Control</u>	<u>Scrubber Sludge</u>	<u>Fly Ash</u>	<u>I</u>
pH <sup>b</sup>	2.6	7.3	9.6	
Al	10	<0.2	0.6	
Fe	107	<0.1	0.2	
Mn	4	2.2	0.04	
Co	1.9	0.7	0.1	
Ni	2.6	0.8	<0.05	
Zn	1.0	0.6	0.02	

<sup>a</sup>Results from interaction of 50 g of attenuating agent with 150 ml of control leachate for 15 h.

<sup>b</sup>Leachate compositions reported as ppm.

TABLE VI  
COMPARISON OF CAPABILITIES OF ELEVEN SORBENTS TO (a) ELEVATE pH AND (b) ATTENUATE THIRTEEN PRIORITY TRACE ELEMENTS IN ILLINOIS BASIN COAL REFUSE LEACHATE

[illegible]

osmosis, chelation and biological treatment.

One of the most promising of these control techniques, alkaline neutralization, is currently used extensively to treat acid drainage from coal mines. While it is well known that alkaline neutralization is very effective in controlling the acid and overall salt compositions of mine waste waters, the degree of control that this method exerts over some of the more highly leachable toxic trace elements remains to be established.<sup>(1)</sup> Elaboration of the latter point is the basis for one of the studies now being conducted in this area.

TABLE VII  
ALKALINE NEUTRALIZATION OF CONTAMINATED  
COAL REFUSE DRAINAGE<sup>a</sup>

	<u>Untreated Leachate Control</u>	<u>Lye</u>	<u>Limestone</u>	<u>Lime</u>
pH <sup>b</sup>	1.1	6	7.1	6.
TDS (%)	0.5	3.4	3.2	3.
Al	18	<0.2	<0.2	<0.
Fe	820	0.06	0.3	0.
Mn	3.6	0.07	6.4	1.
Co	2.0	0.05	1.0	0.
Ni	3.2	0.05	1.0	0.
Zn	3.9	0.02	0.1	0.

<sup>a</sup>Results from addition of alkaline agent to 1l of control leachate until indicated pH was achieved.

<sup>b</sup>Leachate compositions reported as ppm unless otherwise indicated.

trace element contents of them were measured. The results of these experiments are summarized in Table VII.

Examination of Table VII shows that neutralization is an effective technique for decreasing trace element concentrations in refuse waste water. The Cu and Fe contents of the treated solutions are within acceptable limits of the 1977 EPA effluent limitation guidelines for coal preparation plant effluents (Fe  $\leq 3.5$   $\mu\text{g}/\text{mL}$  averaged for 30 days, pH 6-9). Mn, however exceeds the acceptable level of 2.5-3  $\mu\text{g}/\text{mL}$  (averaged for 30 days) in the limestone case. However, this was shown to be due to traces of Mn in the limestone used in the neutralization experiments. Further work in the area of alkaline neutralization of refuse drainage involves its application to more highly contaminated waste water to investigate coprecipitation phenomenon, and the scale up of the process to more life-like circumstances.

### SUMMARY

The purpose of this paper has been to present an overview of research at the Los Alamos Scientific Laboratory to investigate experimentally the more attractive options for controlling trace element contamination of refuse drainages. The control methods under consideration include chemical and physical methods to immobilize or remove undesirable contaminants from refuse disposal, the treatment of refuse disposal sites with attenuation or sealants to prevent the discharge of contaminated water, and the direct treatment of refuse drainage as it emerges from the refuse disposal site. Initial quantitative results from these laboratory studies suggest that the techniques being considered are technically feasible for effectively controlling trace element contamination of refuse dump drainage.

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# MAGNETIC SEPARATION TO COAL RELATED APPLICATIONS

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## Abstract

The cross section for particle collisions with an isolated magnetized fiber in air and water is given as a function of the physical parameters of the filter system. Two models for using the cross section to predict real filter efficiency are discussed. The analysis of particle in air shows a strong dependence of cross section on particle inertia and gravity and pronounced maxima in the cross section at small particle radii, features which are not present in liquids. The cross section in air is especially sensitive to particle size at small particle radii and to the free stream velocity. The cross section in air is reasonably large for a range of conditions, which supports the view that economically practical applications of magnetic filters in air-particle separations may be possible.

separation to filter fine particles was stimulated by the work of Kolm et al. (1,2) The so-called high gradient magnetic separation method was subsequently used for commercial filtration of magnetic impurities from Kaolin. A number of other practical applications were pointed out by Oberteuffer (5) and recently many specific filtration applications in air and liquid streams, including coal related applications have been discussed. (6)

The basic physical idea underlying the operation of gradient type devices is simple: If a ferromagnetic material is placed in a magnetic field it becomes magnetized and attracts particles. Many thin fibers placed transversely to the magnetic field form a fibrous filter which, although supporting a porous structure to allow a relatively free flow of fluid, can carry a substantial load of magnetic impurities.

Work carried out at METC has been concerned with understanding of the basic physical elements of the filtration process. These studies have been on the dynamics of the capture of particles by an isolated fiber and by a fiber in the interior of a regular lattice of fibers. Here we summarize the results and discuss their application to the analysis of the performance of real filters. We consider two different models for calculating the filter efficiency, the isolated fiber model and regular lattice model.

The cross section for capture has been calculated for an isolated fiber and for a fiber in the interior of a regular lattice of fibers. (7) These calculations show that for a highly efficient filter, say fiber spacings greater than eight fiber diameters, the cross section for the isolated fiber and a fiber in the interior of a regular lattice are approximately equal. This does not mean that the interference effects in porous filters, for even though the cross sections may be nearly equal in the two cases, the shadows (in particle density) cast by fibers can significantly affect the efficiency of the filter as a whole. The isolated fiber model neglects entirely the interference, including the shadows, of neighboring fibers, whereas the lattice model considers the fibers as a coherent array and accounts for the effect of the lattice as a whole on particle trajectories. The isolated fiber model gives an optimistic estimate of the efficiency of a real filter whereas the lattice model should provide a low estimate. We discuss first the isolated fiber model and present functional dependence of the clean fiber cross section on the filter parameters. The regular lattice model is discussed in section 3.

## 2. Isolated Fiber Model

In a filter with fiber perpendicular to the stream, the capture distance,  $x_c$ , is the maximum value of the impact parameter for which the particle trajectory intersects the fiber and the

average separation  $\alpha$ , the average number of targets (fibers) is  $1/\alpha^2$ . If the fibers act independently the probability of capture for a particle traveling a depth  $dy$  in the direction of the stream is  $-2x_c dy/\alpha^2$ . The probable change in particle density,  $dn$ , is  $2x_c n dy/\alpha^2$  and it follows that the efficiency of a filter of depth  $y$  is  $1 - \exp(-2x_c y/\alpha^2)$ . These hypotheses explicitly neglect the shadows, i.e., neglect the nonuniformities in particle density in the transverse direction caused by capture of particles from the stream. For particles greater than  $1 \mu m$  we do not expect that diffusion of particles into the shadows is sufficiently rapid to maintain the assumed transverse uniformity.

In the isolated fiber model the cross section is calculated in the approximation which neglects the effect of neighboring fibers. The interference effects are accounted for by introducing an empirical factor, say  $k$ , in the exponent of the efficiency formula. If the fibers are oriented in random directions with respect to the magnetic field, only that fraction of the fibers perpendicular to the field should be counted, which correction may also be absorbed in the empirical factor  $k$ . If the theory is used to represent a filter operating over a period of time, the corrections to the cross section for buildup of particles on the fibers given by Luborsky and Drummond (8) and Watson (9) should be applied.

Even though the empirical correction required to bring calculated and observed efficiencies into agreement is quite large, (8,10,11,12) the isolated fiber model has been useful for identifying the significant physical parameters and for giving roughly correct functional dependence of efficiency on the parameters.

The isolated fiber cross section has been calculated by Watson (13) and Luborsky (4) for inertialess particles and by Lawson et al. (14) for particles with inertia. Usually, particle inertia is negligible for filtration of liquids and significant for filtration of gases, at least for the size range usually considered in magnetic separation. A well known order of magnitude argument shows that the onset of inertial effects should be expected at Stokes number,  $K$ , greater than 0.1. However, even though the shapes of particle trajectories are in fact affected by inertia (14,15) at  $K > 0.1$ , the net effect of inertia on capture cross section is small up to  $K = 1$  for cross sections greater than a fiber diameter.

An idea of the range of particle size and free stream velocity for which particle inertia is negligible may be obtained from figure 1. To the left of the  $K = 1$  curves particle inertia is negligible in the computation of cross sections for cross sections greater than a fiber diameter for a fiber diameter of  $200 \mu m$ .

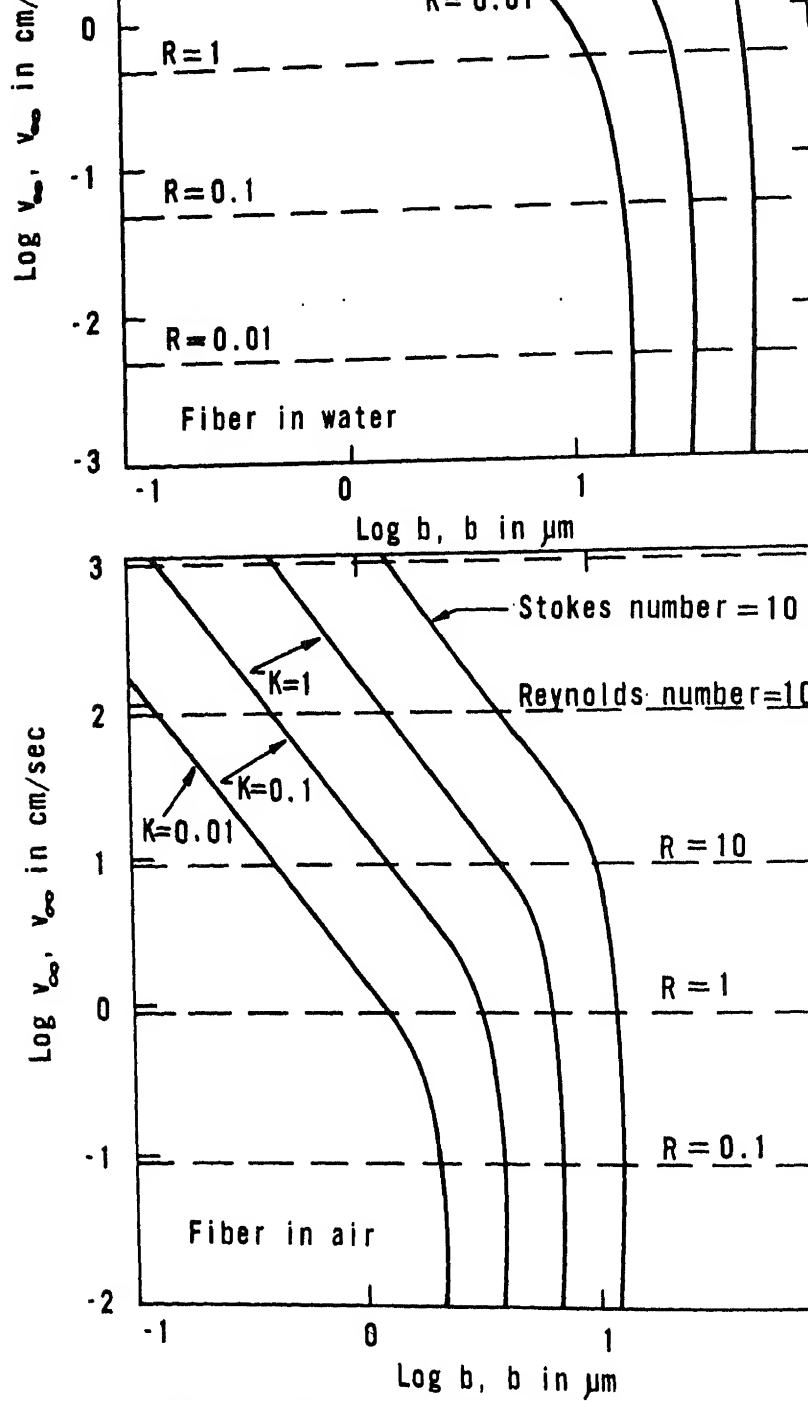


Figure 1.- Curves of constant Stokes number and constant Reynolds number for a 200  $\mu\text{m}$  diameter fiber in water and air.



n, indicates whether fluid viscosity is significant in determining the flow field. For Reynolds number greater than potential flow, which neglects fluid viscosity, is probably an adequate representation of the flow on the front side of isolated fiber. Below  $R = 10$ , potential flow misrepresents fluid field, but for cross sections greater than a fiber meter the error incurred by this approximation may not be excessive.

The isolated fiber cross section has been calculated for a broad range of conditions which include filtration. For conditions such that particle inertia and the gravitational force are negligible, the cross section depends on a single dimensionless parameter.<sup>(13)</sup> This parameter is the ratio of a magnetic quantity,  $v_m$ , with the dimensions of velocity and the free stream velocity  $v_\infty$ . Increasing  $v_m$ , either by increasing  $v_m$  or decreasing  $v_\infty$ , increases the cross section.

When particle inertia and the gravitational forces are significant, the cross section is a function of three dimensionless parameters,<sup>(14,15)</sup>  $v_\infty/v_T$ , the Stokes number and  $v_m/v_T$ , where  $v_T$  is the terminal velocity of a particle falling parallel to the free stream. The expressions for the significant parameters are

$$v_T = v_\infty + \frac{2\rho_p b^2 g(\rho_p - \rho_f)}{9\eta} ,$$

$$v_m = \frac{2\chi B b^2 M}{9(1+\chi/3)\eta a} ,$$

$$K = \frac{2b^2 \rho_p v_T}{9\eta a} .$$

There are nine physical quantities involved here, the particle properties,

$\rho_p$ , mass density,

$b$ , radius,

$\chi$ , magnetic susceptibility,

the fluid characteristics,

$\rho_f$ , mass density,

B, the external magnetic field strength.

The dependence of cross section on the dimensional parameters  $v_m/v_T$ ,  $K$  and  $v_\infty/v_T$  is shown in figures 2 and 3. There have been observations of trajectories and cross sections for particles in air<sup>(15)</sup> which are in agreement with the cross sections shown here, which provides a check on the theory for a small range of the parameters considered.

The cross section is shown in figures 4 to 11 as a function of the physical parameters  $B$ ,  $b$  and  $v_\infty$ . The cross sections are for particles in air and water for low, moderate and high particle susceptibility. As discussed above, in the fiber model, the cross section is used to calculate the efficiency from the expression

$$\text{efficiency} = 1 - \exp\left\{-\frac{k^2 X_c a y}{a^2}\right\},$$

where  $X_c = x_c/a$  is the cross section in units of the diameter. Taking  $k = 1$  neglects fiber orientation and interference effects entirely and provides an upper bound on the efficiency of a real filter. In section 4 we will discuss certain prominent features of the cross section curve. First we consider the lattice model of a filter.

### 3. Regular lattice of Fibers.

We give now a brief description of the regular lattice model and the results of the calculation of trajectories and cross section. The details of the analysis and full account of the results are given in reference 7. The lattice consists of parallel circular fibers with fiber axes perpendicular to the magnetic field. The fluid flow and gravitational field are parallel and directed oppositely to the magnetic field. Rectangular and rhombic lattices have been studied.

The external magnetic field magnetizes the fibers. Each fiber acquires a uniform magnetic moment per unit length in the direction of the magnetic field. The resultant field is the external field plus the field caused by the magnetized fibers. The fluid field is the sum of the uniform flow and the fluid disturbances caused by the circular fibers. We have developed analytical expressions for the resultant fields which represent a lattice with its longest dimension in the direction of the field. From these expressions we calculate the forces on a magnetic particle in the interior of a lattice.

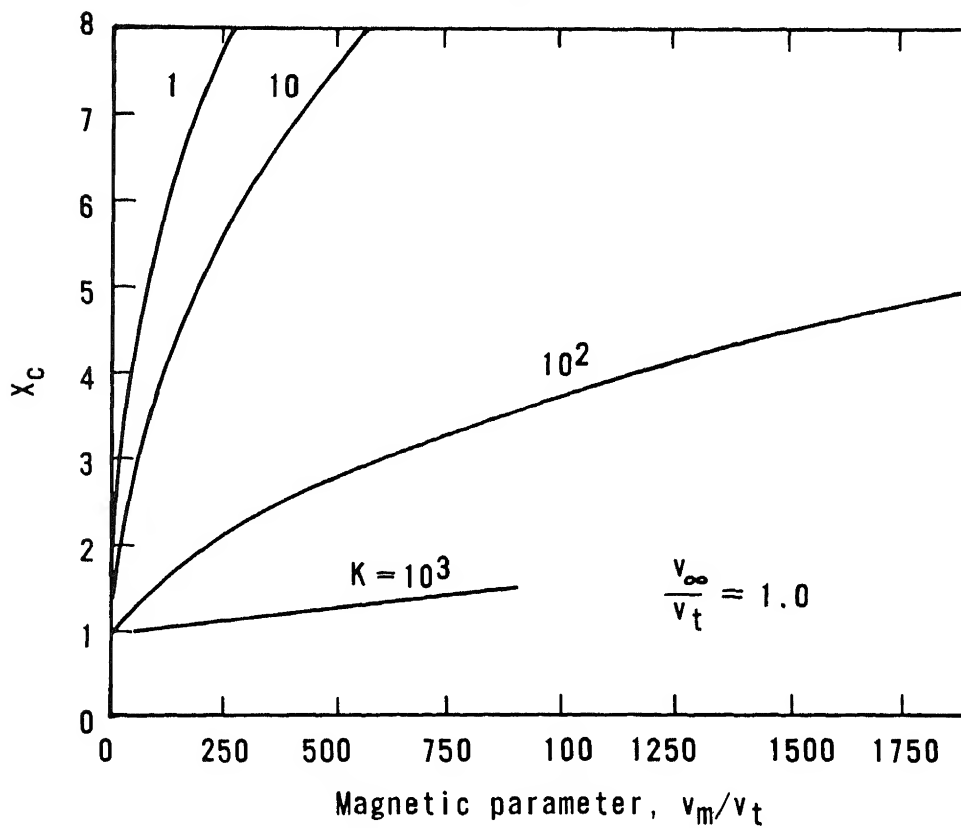
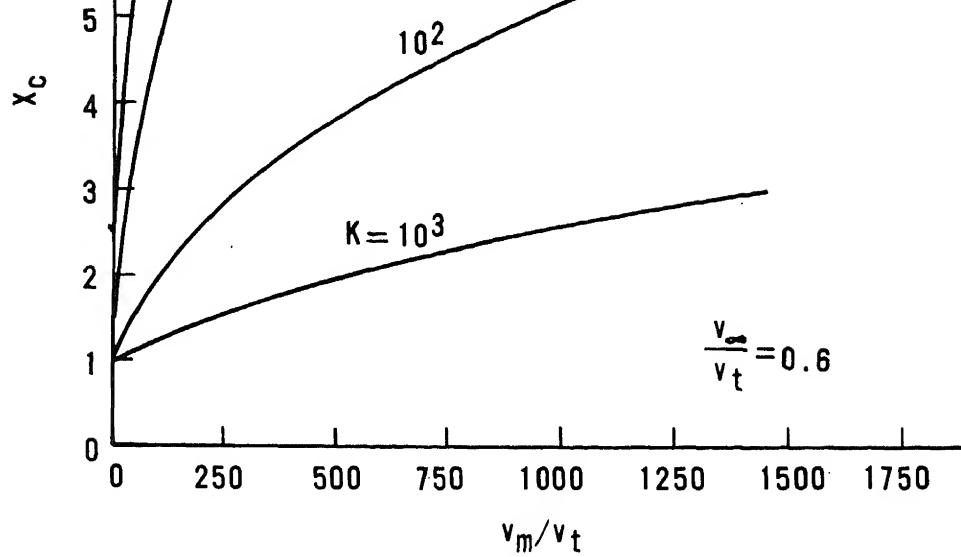


Figure 2.- Cross section as a function of  $v_m/v_t$  for fix Stokes number,  $K$ , and gravitational parameter  $v_\infty/v_t$ .

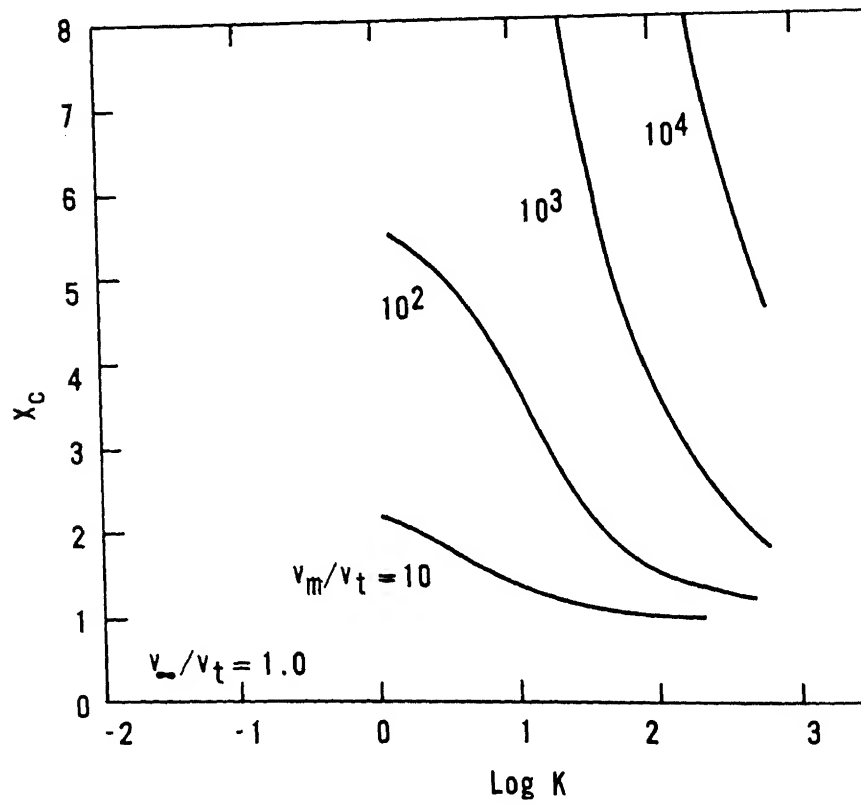
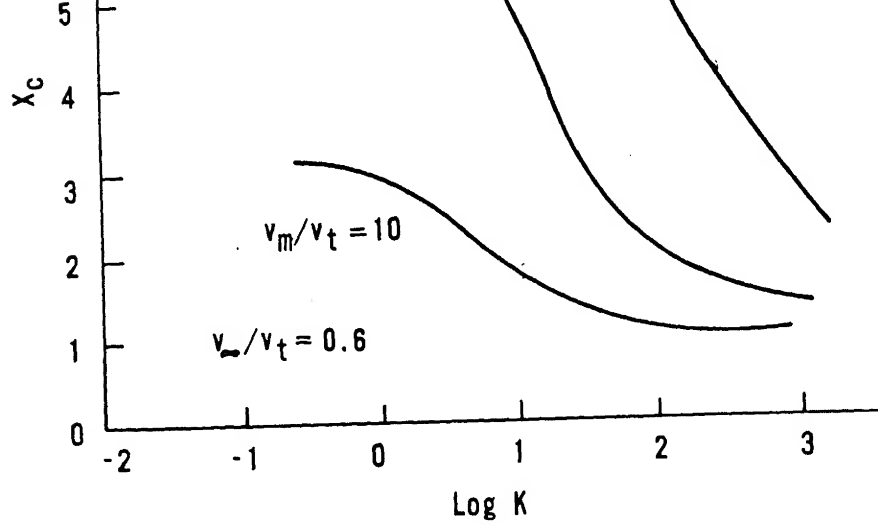


Figure 3. - Cross section as a function of Stokes number for fixed magnetic parameter and gravitational parameter

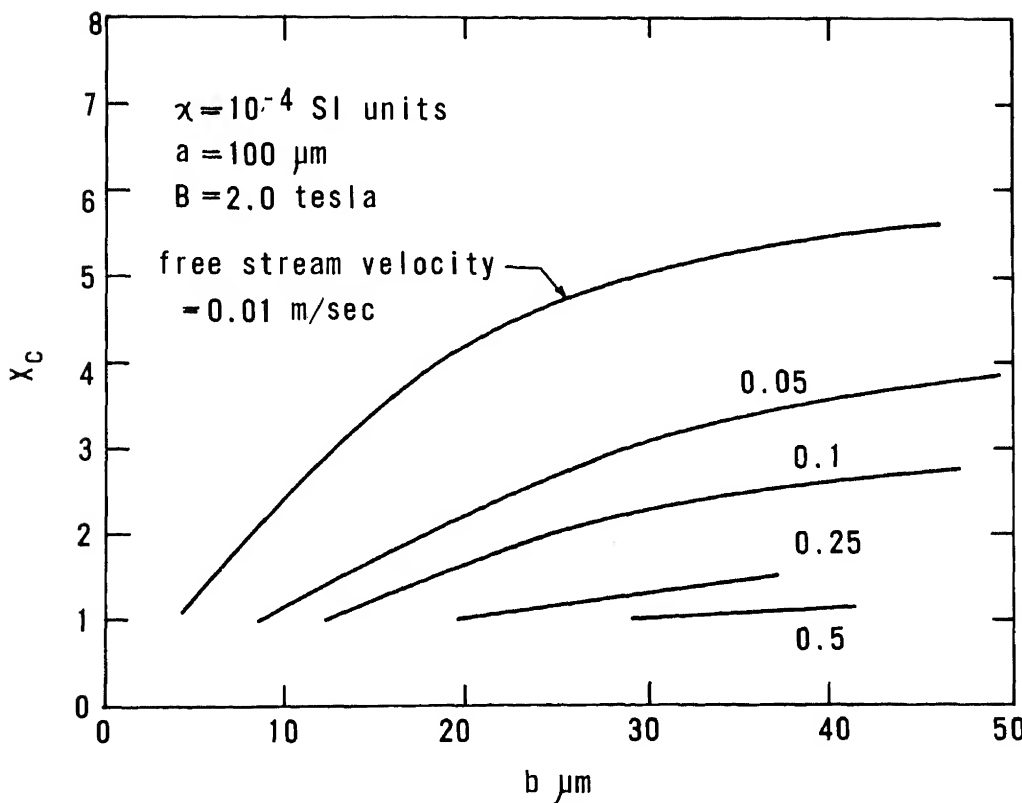
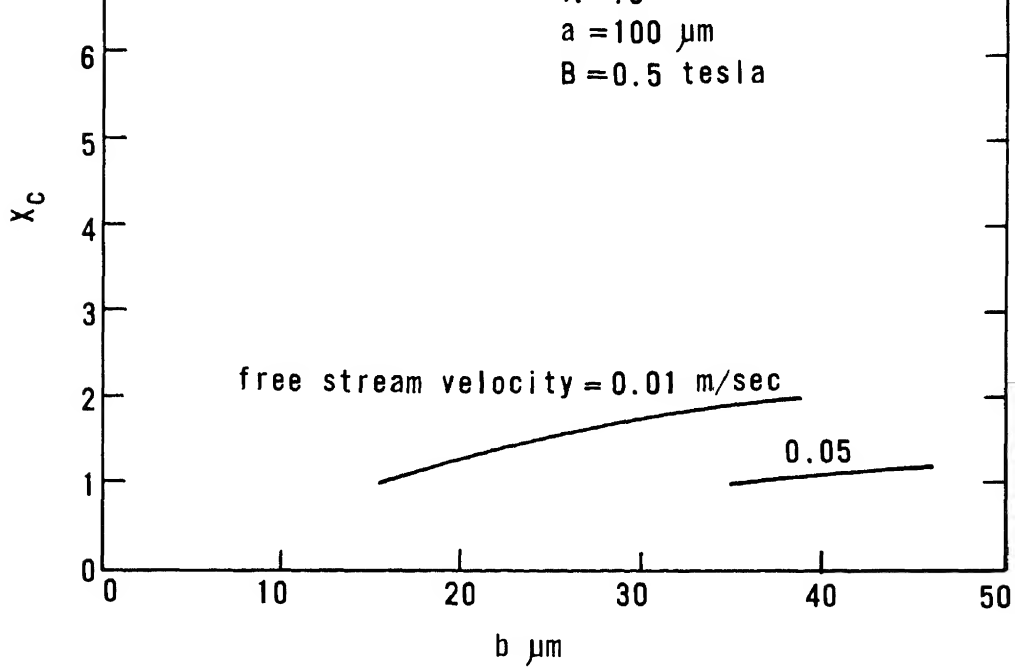


Figure 4.- Cross section in water as a function of particle size  $b$ , parametrized by the free stream velocity,  $v_\infty$ , for fixed low

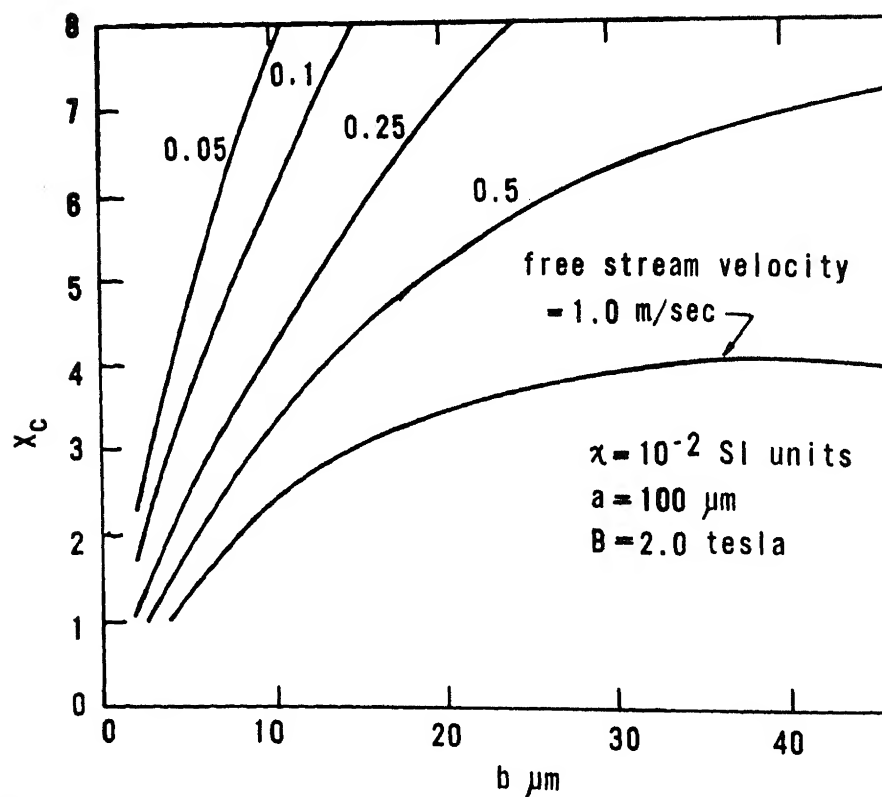
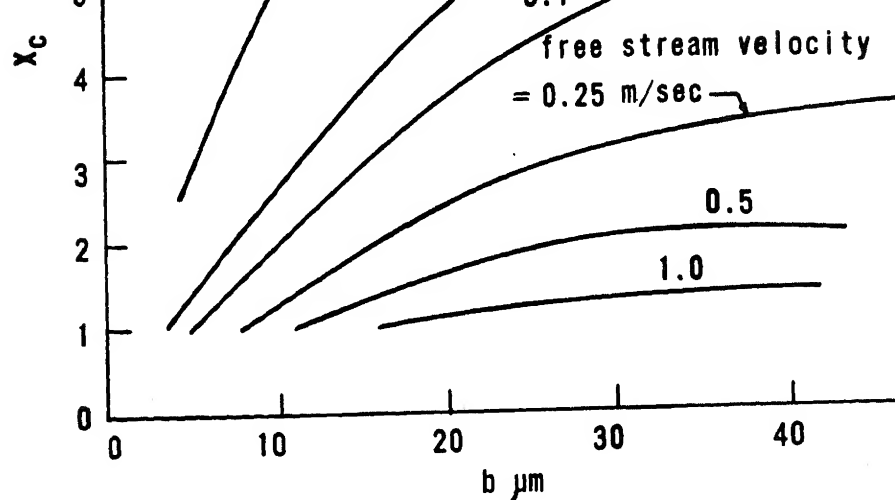


Figure 5.- Cross section in water as a function of particle size  $b$ , parametrized by the free stream velocity,  $v_\infty$ , for fixed particle susceptibility,  $\chi$  and two values of the magnetic field,  $B$ .

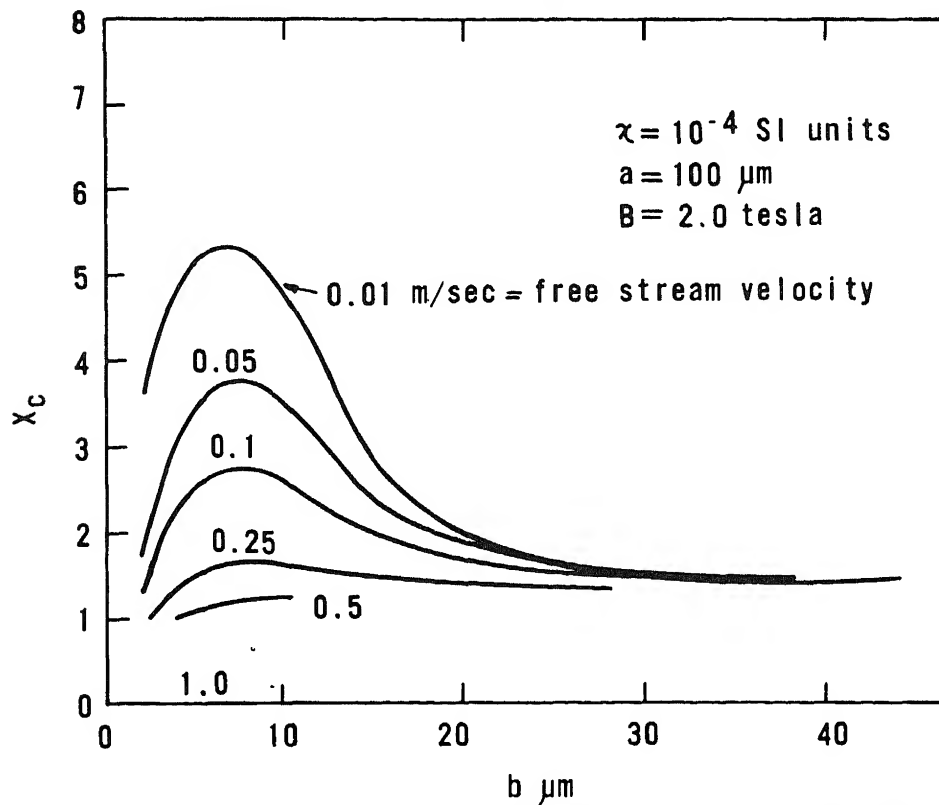
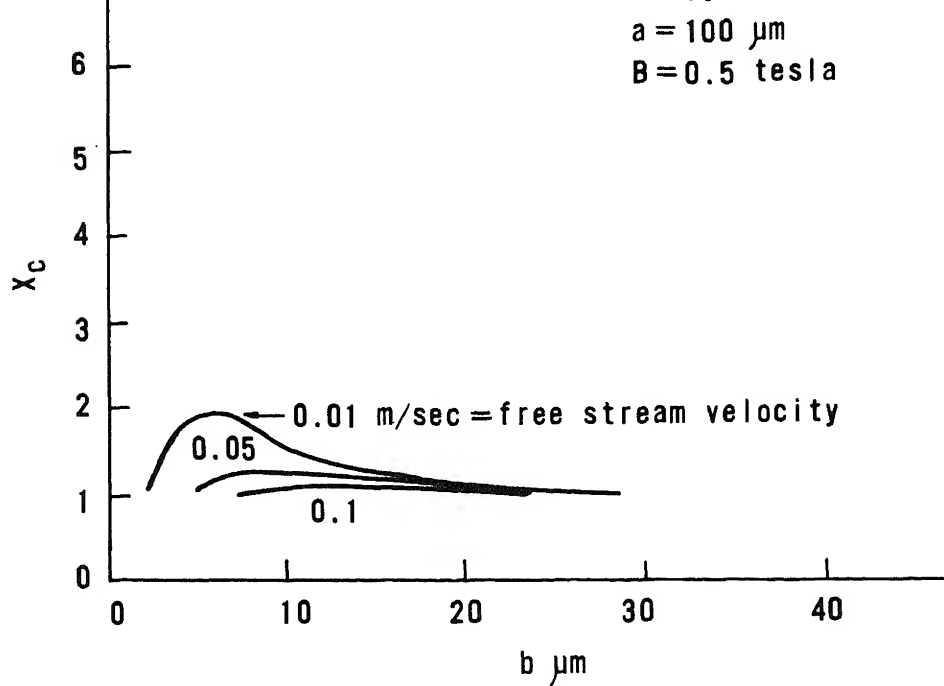


Figure 6. -- Cross section in air as a function of part  
 radius, parametrized by the free stream velocity,  $v_\infty$ ,

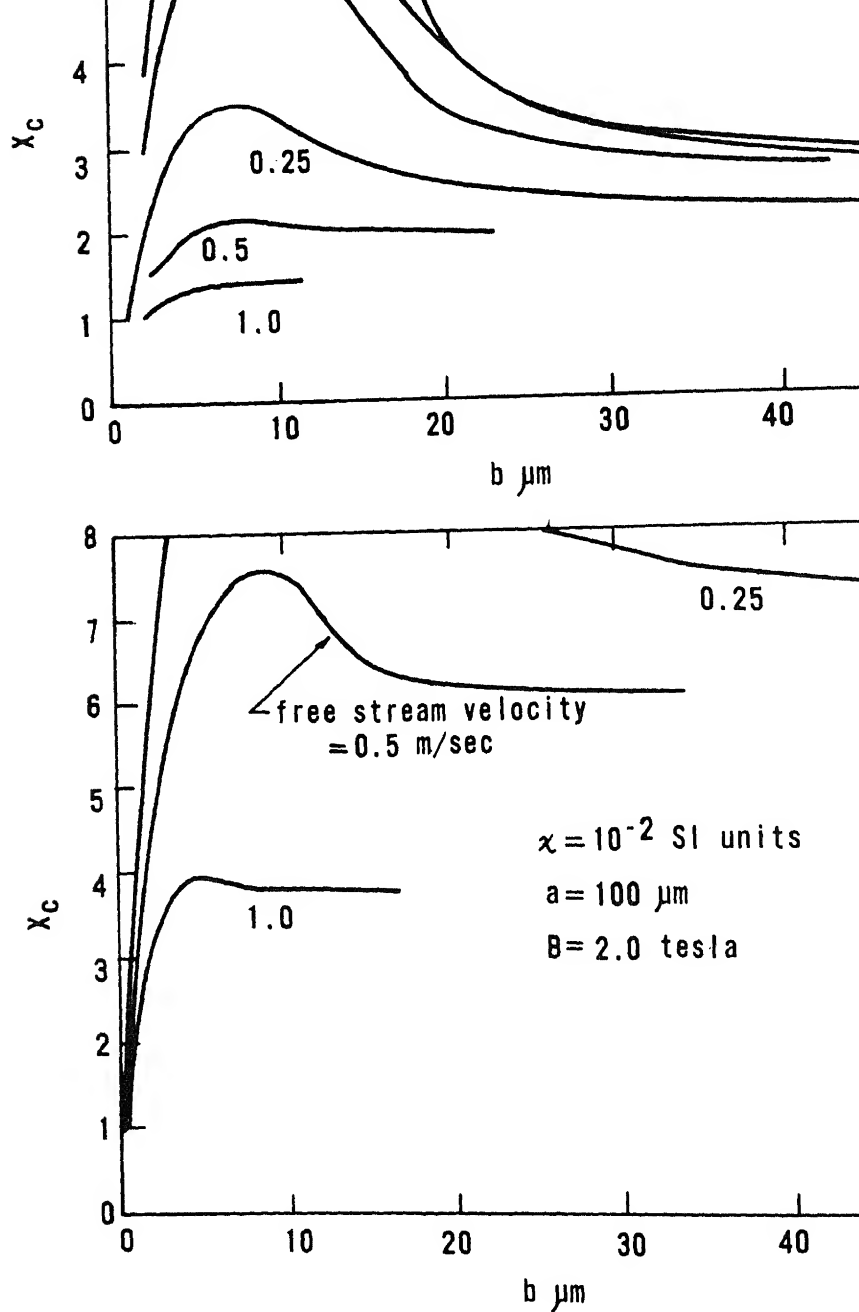


Figure 7. - Cross section in air as a function of radius, parametrized by free stream velocity,  $v_\infty$ , high particle susceptibility  $\chi$  and two values of magnetic field  $B$ .



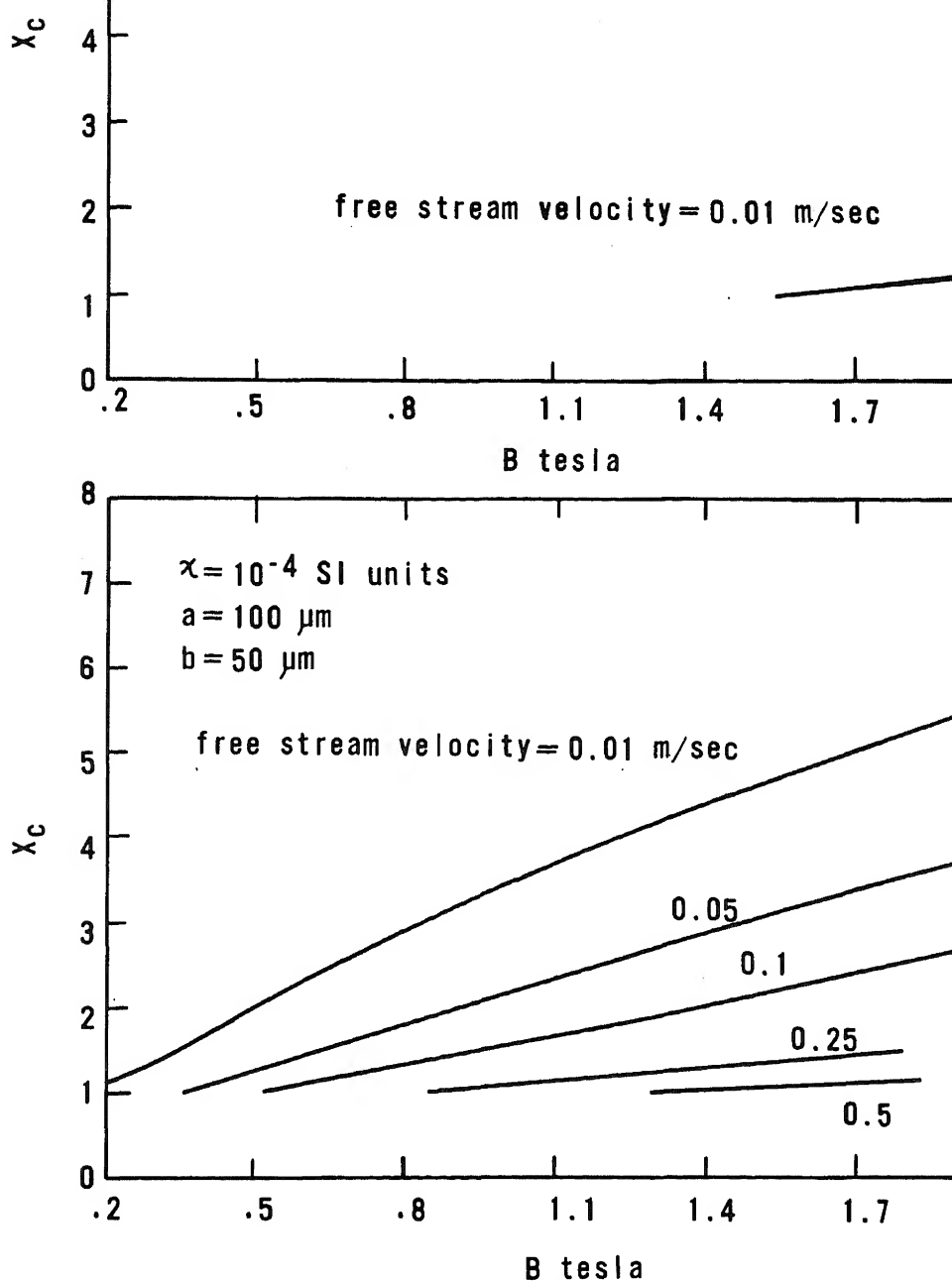


Figure 8.- Cross section in water as a function of magnetic field, parametrized by the free stream velocity,  $v_\infty$ , for low particle susceptibility and two particle radii.

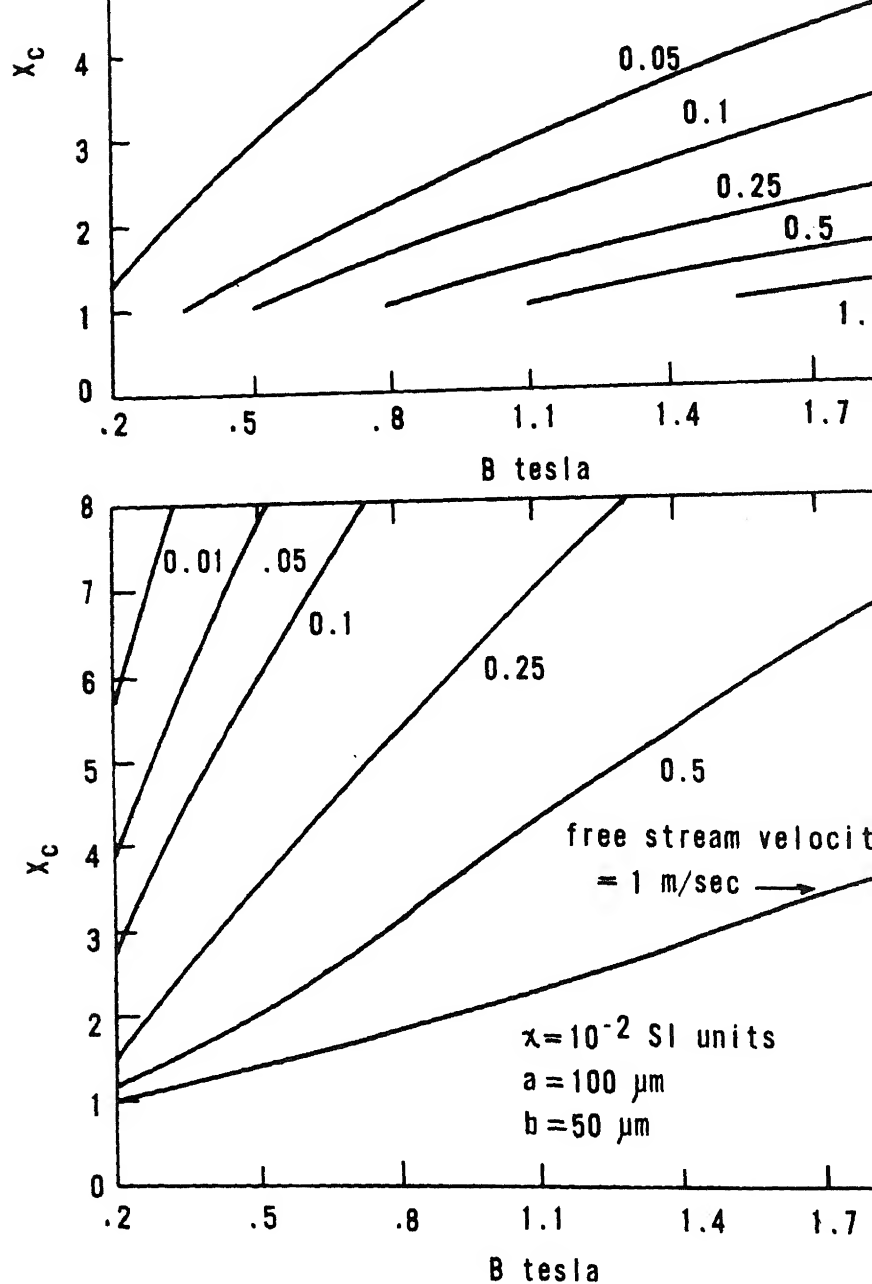


Figure 9.- Cross section in water as a function of magnetic field, parametrized by the free stream velocity,  $v_\infty$ , fixed high particle susceptibility and two particle

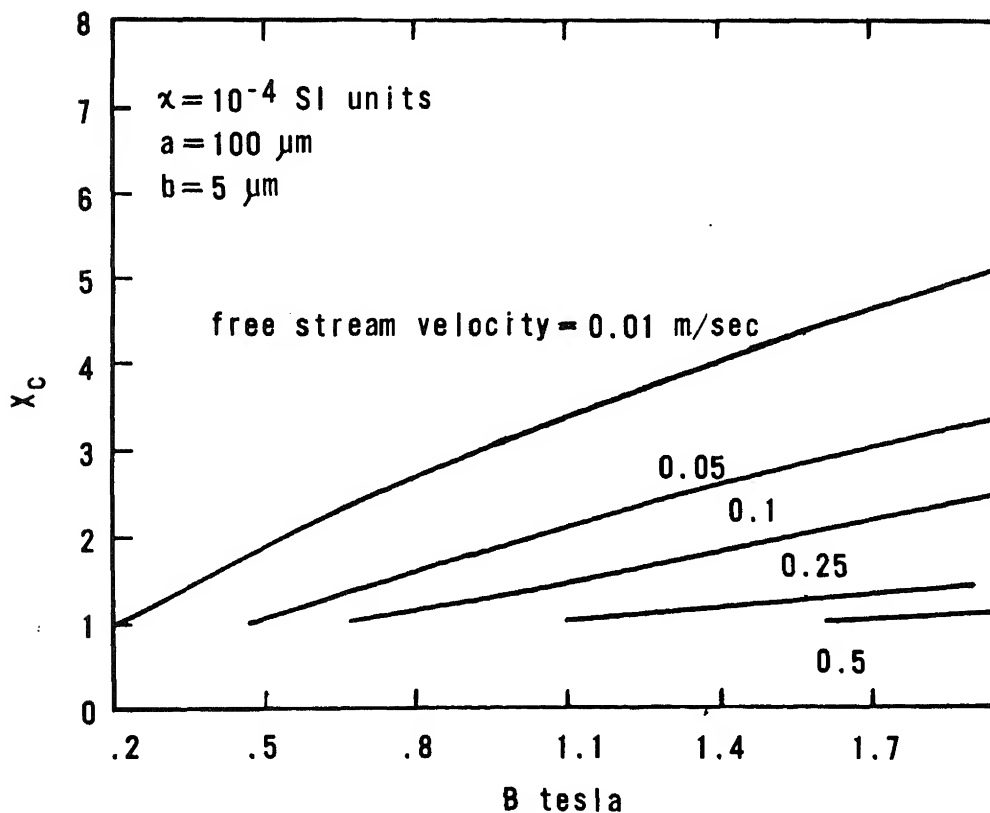
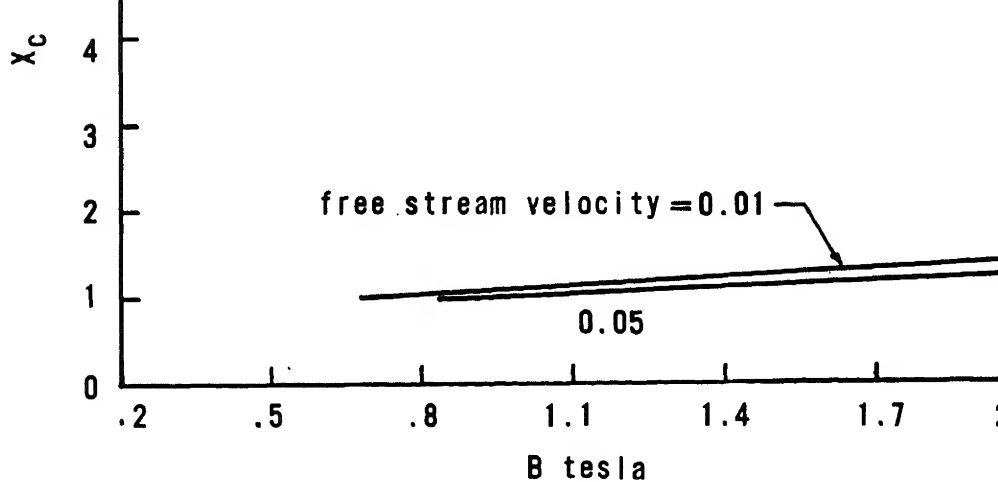


Figure 10.- Cross section in air as a function of magnet field, parametrized by the free stream velocity,  $v_\infty$ , for low particle susceptibility and two particle radii.

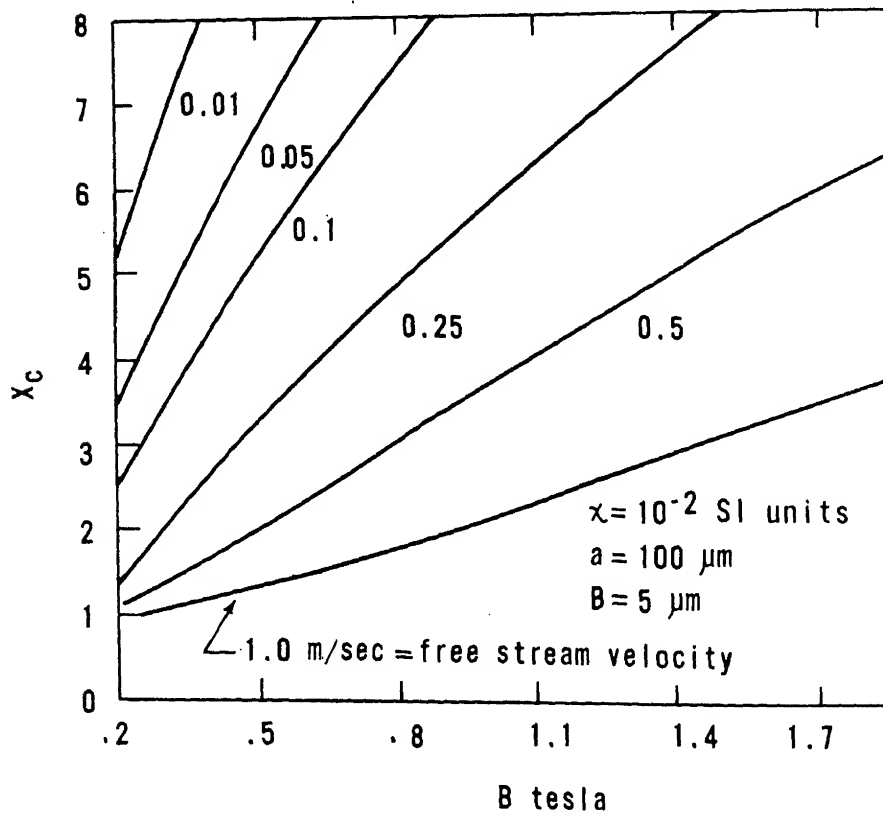
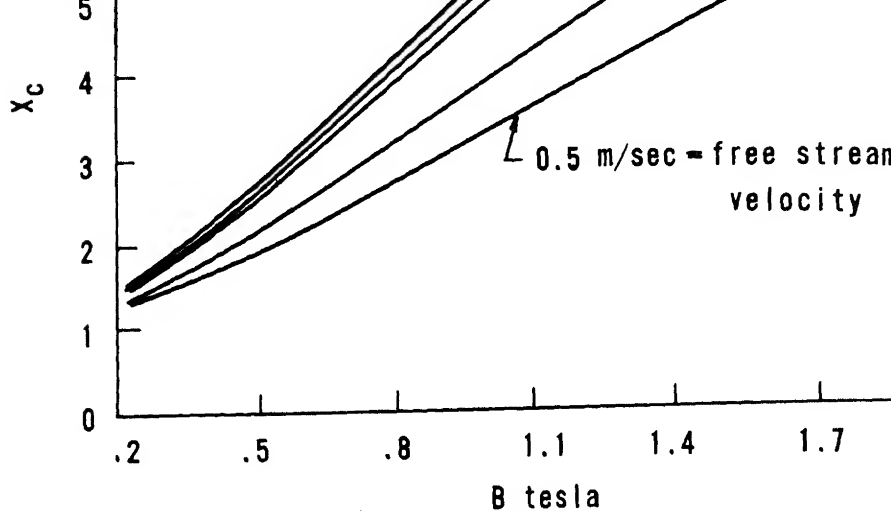


Figure 11.- Cross section in air as a function of mag field, parametrized by the free stream velocity,  $v_\infty$ , high particle susceptibility and two particle radii.

The equation has been integrated in the approximation which neglects particle inertia, and trajectories and cross sections have been obtained. The cross section is shown in figure 12 as a function of  $v_m/v_T$  for a fixed horizontal distance between fibers and different spacings in the vertical direction both rectangular and rhombic lattices. Multiplication of the cross section shown in figure 12 by  $\alpha/2a$ , where  $a$  is the radius, gives the cross section in units of fiber diameter. This allows a comparison with the isolated fiber cross section. For fiber separations  $\alpha/a \geq 8$ , the isolated fiber and the lattice cross section are not greatly different.

Particle trajectories in the rhombic and rectangular lattices are shown in figure 13. Because of the periodicity of the force field the pattern of trajectories found in one cell will be repeated throughout the lattice. It is seen that trajectories are separated into those which intersect the fibers and those which do not. Trajectories which enter an upper cell boundary and do not get captured will leave that cell and enter the cell below. Since this pattern is repeated these trajectories will not intersect any of the fibers below. Thus, escape channels are formed which permit particles to pass through the filter. The width of the channel depends on  $v_m/v_T$  and can be made as narrow as one please by increasing  $v_m/v_T$ , e.g. by increasing the magnetic field.

One sees at this point an essential difference between the filter efficiencies of the isolated fiber and the lattice models. Assuming a horizontally uniform distribution of particles entering the lattice the number of particles passing through the filter is proportional to the width of the escape channel, which is  $\alpha - 2x_c$  in the case of the rectangular lattice. The filter efficiency is thus, simply,  $2x_c/\alpha$ . A similar result holds for the rhombic lattice. As noted above the limiting case  $2x_c/\alpha = 1$ , which implies an impenetrable fiber layer, can be obtained for sufficiently large  $v_m/v_T$ . It is not surprising that the lattice efficiency is independent of filter depth in contradistinction to the exponential dependence obtained from the isolated fiber model.

We expect that the lattice model gives a low estimate of real filter efficiency. The regularity and complete coherence of fibers in the lattice probably includes the effects of shadows rather too strongly, whereas, the isolated fiber viewpoint neglects completely the fiber shadows. A better description would seem to lie somewhere between the two models.

#### 4. Discussion

The dependence of the cross section on the parameters of the system is shown in figures 4 to 11. The cross section is used to compute the efficiency of a clean porous filter

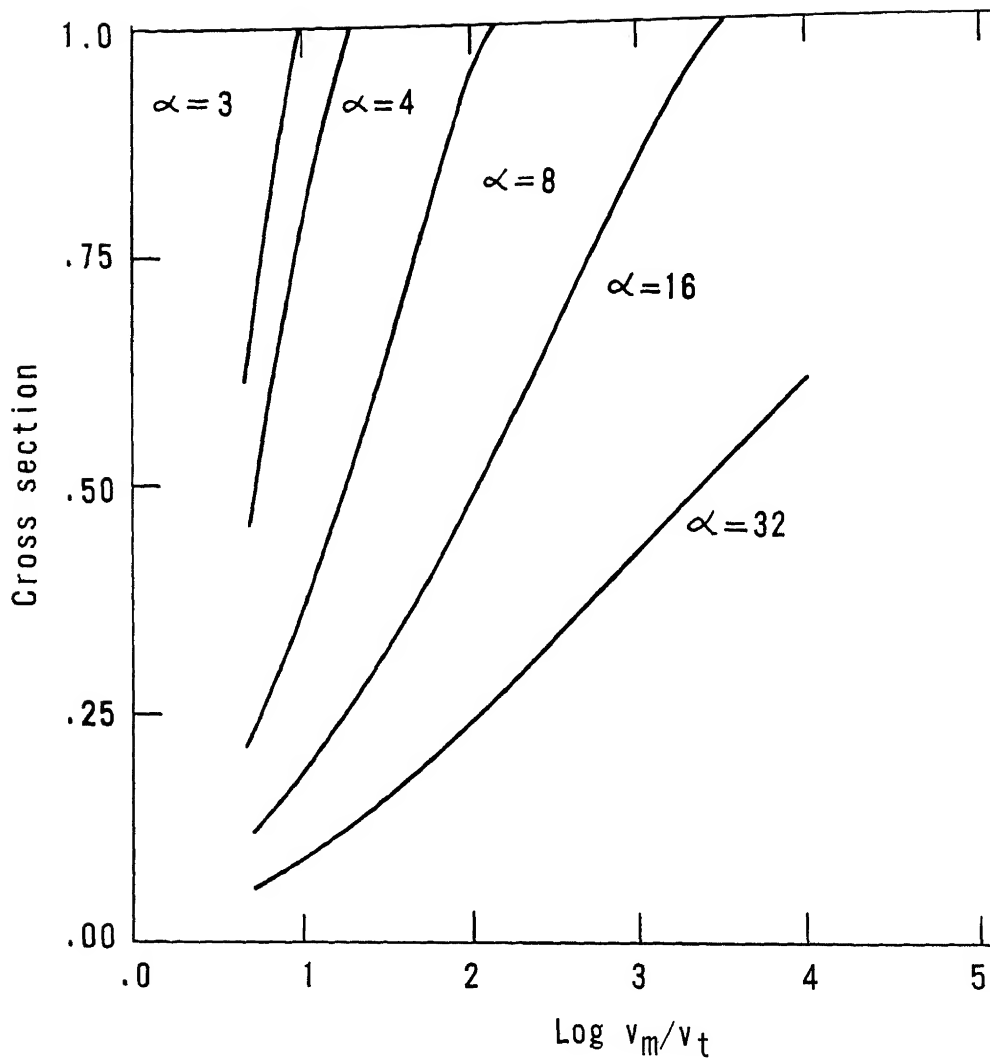


Figure 12.- Cross section for a fiber in rectangular I function of magnetic parameter with horizontal distance fibers fixed at  $\beta=8$ .

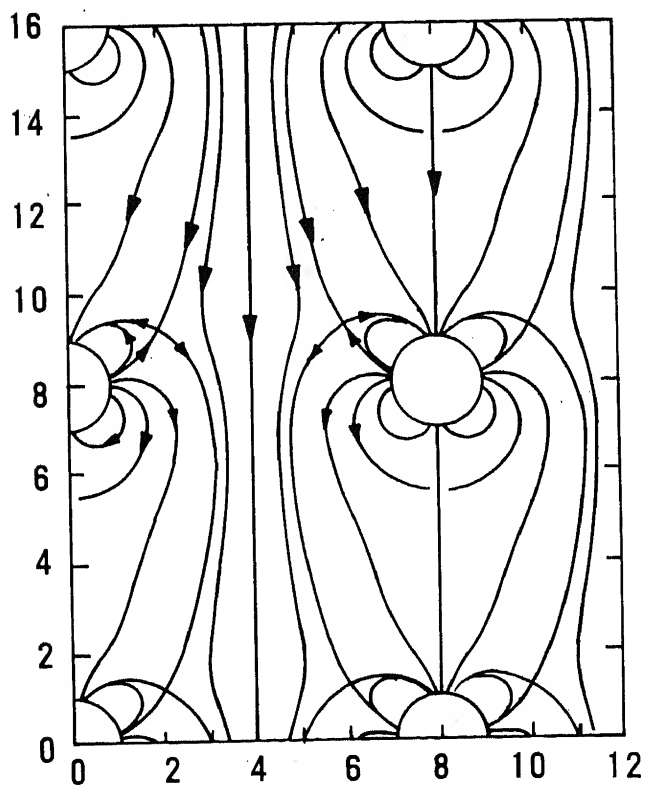
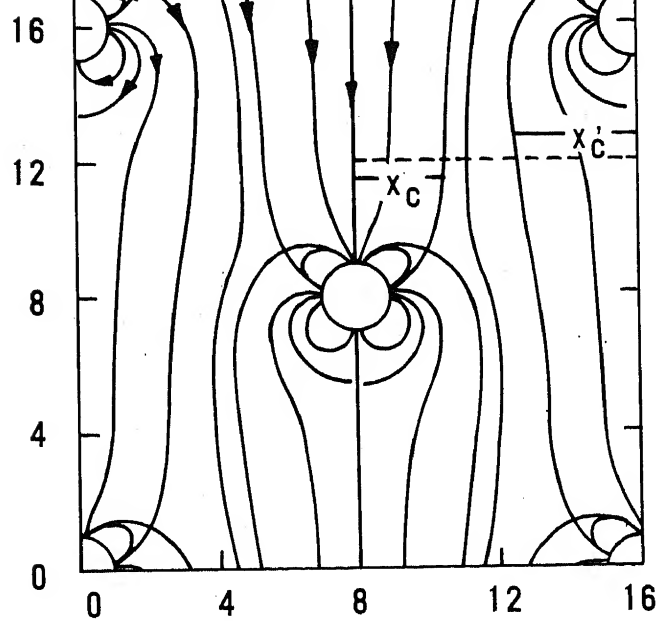


Figure 13.- Particle trajectories in 8x8 square and rhombic lattices showing escape channels.

Figure 1 shows that the parameter  $v_\infty/v_T$  is a measure of the magnitude of the parameter  $v_\infty/v_T$  is a measure of the magnitude of the gravitational force. For example, if  $v_\infty/v_T = 1$  is no gravitational effect and  $v_\infty/v_T = 0$  corresponds to particle falling past a fiber in still fluid.

The cross section as a function of Stokes number, metrized by the magnetic parameter, is shown in figure One sees the strong decrease of cross section with Stokes number at large Stokes number. This behavior makes it difficult to obtain large cross sections in air at high free velocities. However, at moderate and low velocities it is not hard to obtain rather large cross sections. For example, in air for a moderate particle susceptibility,  $\chi = 10^{-1}$  units, magnetic field  $B = 1.0$  tesla, particle radius  $1 \mu m$  and iron fibers of radius  $a = 100 \mu m$ , we obtain from the expression on page 4,  $v_m = 18$  m/sec. Then if  $v_\infty = 0.2$  we have  $v_m/v_T = 54$ ,  $v_\infty/v_T = 0.6$  and  $K = 47$ , the latter being in the inertial range. Referring to the upper graph in figure 3 (or figure 2) we obtain a cross section of two fiber diameters.

Figures 2 and 3 and the numerical example illustrate a point which has already been appreciated, for example, Gooding et al. (11): The flow velocity is an especially important parameter in the magnetic filtration of air. It is also important in liquids, but in air higher velocities are generally required and the cross section decreases with increasing velocity by virtue of a decrease in the magnetic parameter and an increase in Stokes number. Whereas, in the inertialess condition, typically realized in liquids, the Stokes number dependence is absent.

Figures 4 to 7 show, for air and water, the dependence of cross section on the particle radius. It is often noted that high gradient magnetic separation is especially suited to the filtration of fine particles. Although this method may be better than others one nevertheless notes that in water there is a monotonic increase of cross section with particle size and the capture of the larger particles.

In air, where inertia is important, both  $v_m/v_T$  and  $K$  increase with increasing  $b$  and the competing effects result in pronounced maxima in the cross section shown in figures 6 and 7. Roughly speaking, the maxima are caused by the increase in  $v_m/v_T$  with  $b$  at small  $b$  and the increase in  $K$  at minimal velocity and particle inertia having a dominant effect at high  $b$  and bringing the cross section down.

The monotonic increase of cross section with the magnetic field shown in figures 8 to 11 is simply due to the increase in the magnetic parameter when the other parameters are



The theoretical cross section for the collision of particles with magnetized fibers is given as a function of the physical parameters of the filter system. The cross section for particles in liquid is well known and the graphs for water given here show only additional details of the functional dependence on the parameters. The relatively large cross sections found in liquid have encouraged the investigation of practical applications. The results presented here for particles in air extend existing results. The cross sections are reasonably large for an interesting range of conditions which supports the view that filtration of fine particles in air may be economically practical.

Unfortunately it is not possible, at this time, to predict with reasonable accuracy the efficiency of a real filter with the aid of the isolated fiber cross section. It is suggested that the interference effects in real filters are very important and are not accounted for correctly either by the isolated fiber model or the lattice model. Nevertheless the isolated fiber cross section has been a reliable indicator of the qualitative behavior of real filters. In air the conclusion is that the fiber cross section and hence the filter efficiency is very sensitive to free stream velocity, and the cross sections will be relatively low for applications which require moderate magnetic fields and free stream velocities of 1 m/sec and larger. Of course filter efficiency can always be increased by increasing the density of fibers and decreasing the filter but only at the expense of pressure drop across the filter. The analysis in air also shows maxima in the cross section at about 10  $\mu\text{m}$  which are not present in liquid. The maxima are very pronounced at low velocities and tend to disappear as the free stream velocity is increased.

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## INTRODUCTION

Coal production is expected to increase significantly over the 20-year period with coal serving as the primary fuel for electrical generation, replacing dwindling supplies of domestic oil and gas, and reducing dependence on expensive imported oil and gas. Coal production will increase to meet the needs of the emerging gasification and liquefaction industries. The increased tonnage will be from new mines or from expansion of existing mines; many of these mines will be (or are) located in coal fields east of the 100th meridian. This line, lying east of the North Dakota lignite field and west of the Texas coal fields, roughly divides the country into two regions: a western region of low-sulfur coal where rainfall is usually less than 26 inches/year, and an eastern region where rainfall generally exceeds 26 inches/year and most of the coal (lignite excepted) as well as the rocks overlying the coal, often has a relatively high sulfur content. Sulfur in the eastern region is primarily in the form of iron pyrite. Mining eastern region coals exposes the pyrite to oxidation, producing ferrous sulfates which produce acid upon hydrolysis. The acid water is pumped from the mine and, unless effectively treated, leads to environmental degradation of streams and lakes within the watershed and a potential health hazard from a polluted drinking water supply.

In early FY 76 a program was begun at Argonne National Laboratory (ANL) to evaluate technologies for controlling the environmental impacts of coal effluents resulting from the surface mining of coal. The program is being performed for the Department of Energy's Division of Environmental Conservation Technology (DOE-ECT) as part of ECT's overall mandate to assess the effectiveness of methods for controlling pollutant emissions from energy extraction, conversion, and utilization processes. Initial support for this study is "pass-through" funding from the U.S. Environmental Protection Agency; current support comes from DOE-ECT.

This program has a twofold purpose which is related in part to the interests of its two federal sponsors. The overall issue addressed by the sponsors is the need to satisfy increased coal demand in an environmentally acceptable manner. Each sponsor, however, has particular objectives. The EPA is interested in an evaluation of the efficacy and practicability of coal mine effluent control options currently in use, an identification of future technology needs, and recommendations for research. The EPA is also interested in an assessment of the validity of the recently promulgated effluent discharge limits for the coal mining industry, with this assessment emphasizing the effects of climatic variation impacts on effluent quantity and quality. A program plan was outlined to: (1) project future coal production levels to the year 2000 as a basis for selection of case study sites; (2) gather data on

The results of this program are providing data for federal and industrial decision-makers concerned with: (1) developing criteria for choosing the "best" environmental control option; (2) policy decisions involved in the siting of future coal facilities; and (3) establishing basis for national judgments on the practicability of present and anti environmental standards.

The program interacts with the National Coal Association, 15 companies, 12 universities, and 10 state and federal regulatory/research agencies.

## PROGRAM PLAN

This program is focused on the assessment of alternate control technologies that show promise for environmentally safe handling of effluents and wastes from strip mining operations in the eastern region (east of 100th meridian) coal fields through the end of the century. The program has been divided into five tasks, and a unit operations master plan developed which shows the interrelationship of the tasks (Fig. 1):

### TASK 1 - FUTURE COAL PRODUCTION SCENARIOS AND CASE STUDY SITE SELECTION

In this effort ANL estimated future coal production levels through the year 2000 and identified areas east of the 100th meridian where surface coal production is expected to increase. A series of maps was produced showing each state's coal fields, active mines producing over 200,000 tons per year, and proposed new mine openings. A series of computer-drawn maps of each state's coal reserves also was completed; these maps show total, surface, and deep minable reserves for each county where data is available. From these maps and from contacts with the National Coal Association, industry sources, and the U.S. Bureau of Mines, twenty-one areas were chosen as the most promising places for increased production. Mines were selected for each area which typified local coal field conditions. Permission was obtained from mine company officials to use the mines as case study sites from which data could be gathered regarding the volume and character of mine effluent discharge.

### TASK 2 - MINE DRAINAGE GEOCHEMISTRY

An intensive sampling program was developed to determine the volume and characteristics of mine effluents at each of the twenty-one case study mines. All mines were coded to shield their identity. Consultants under Argonne supervision conducted sampling activities; samples were obtained at the mine pit discharge point before any treatment and at the treatment plant charge point, thus obtaining a measure of the treatment efficiency. Samples

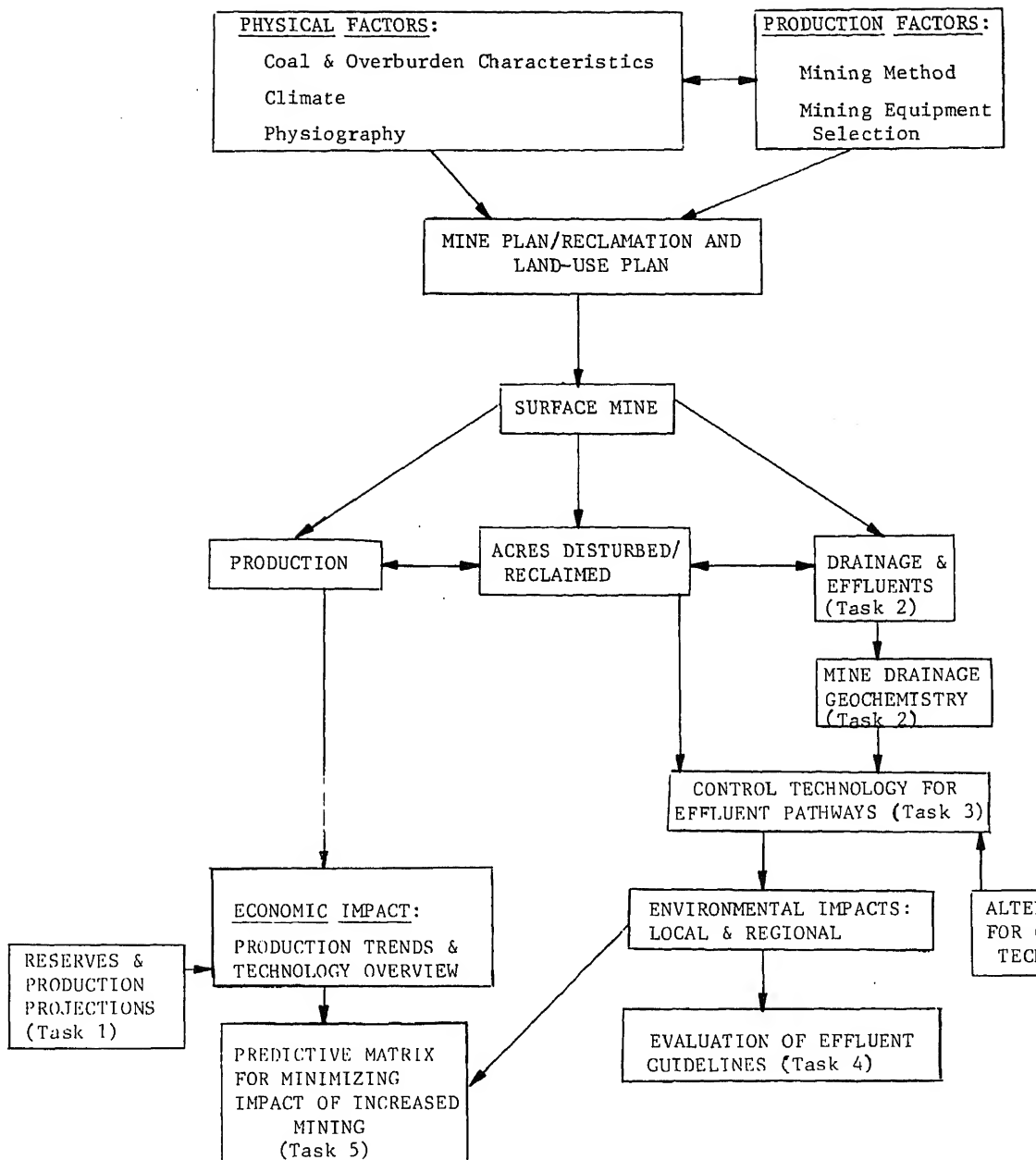


Fig. 1. Unit Operations Master Plan

Conductivity	Aluminum
pH	Sulfate
Dissolved oxygen	Chloride
Acidity/alkalinity	Fluoride
Total dissolved solids	Strontium
Total suspended solids	Magnesium
Iron	Ammonia
Sodium	Potassium

Trace element analysis was performed every three months. Elements analyzed included:

Mercury	Vanadium
Cadmium	Molybdenum
Cobalt	Nickel
Chromium	Lead
Copper	Zinc

The overburden was sampled and analyzed for major, minor, and trace elements, and forms of sulfur. Coals were sampled and underwent proximate and ultimate analyses in addition to the same types of analyses performed on the overburden. Acid potential (derived from pyritic sulfur) and neutralization potential were also determined.

The field sampling phase has been completed and the data are being reviewed and analyzed. Argonne is analyzing the sample data and assessing the environmental impacts and pollution potential for each site. This information, coupled with the information relative to the increased coal production and control technology options, will provide the baseline data for a study on the potential environmental impacts related to increased surface mining through the end of the century. Figure 2 summarizes the various operations for Task 2.

### TASK 3 - CONTROL TECHNOLOGY ASSESSMENT

Mine effluent quality is being examined before and after treatment to provide a measure of the effectiveness of the treatment process. Process technology cost data are being obtained whenever possible. Process waste products are being identified and characterized, and the economics of disposal/reclamation are being considered. The environmental impact of waste products generated by the various treatment process and selected alternative processes are being studied. Figure 3 indicates the identified unit operations for control technology assessment at surface coal mine.

A data management system for computer storage of the data generated under this program has been selected and implemented. All relevant storage and retrieval systems were reviewed, and System 2000 was selected.

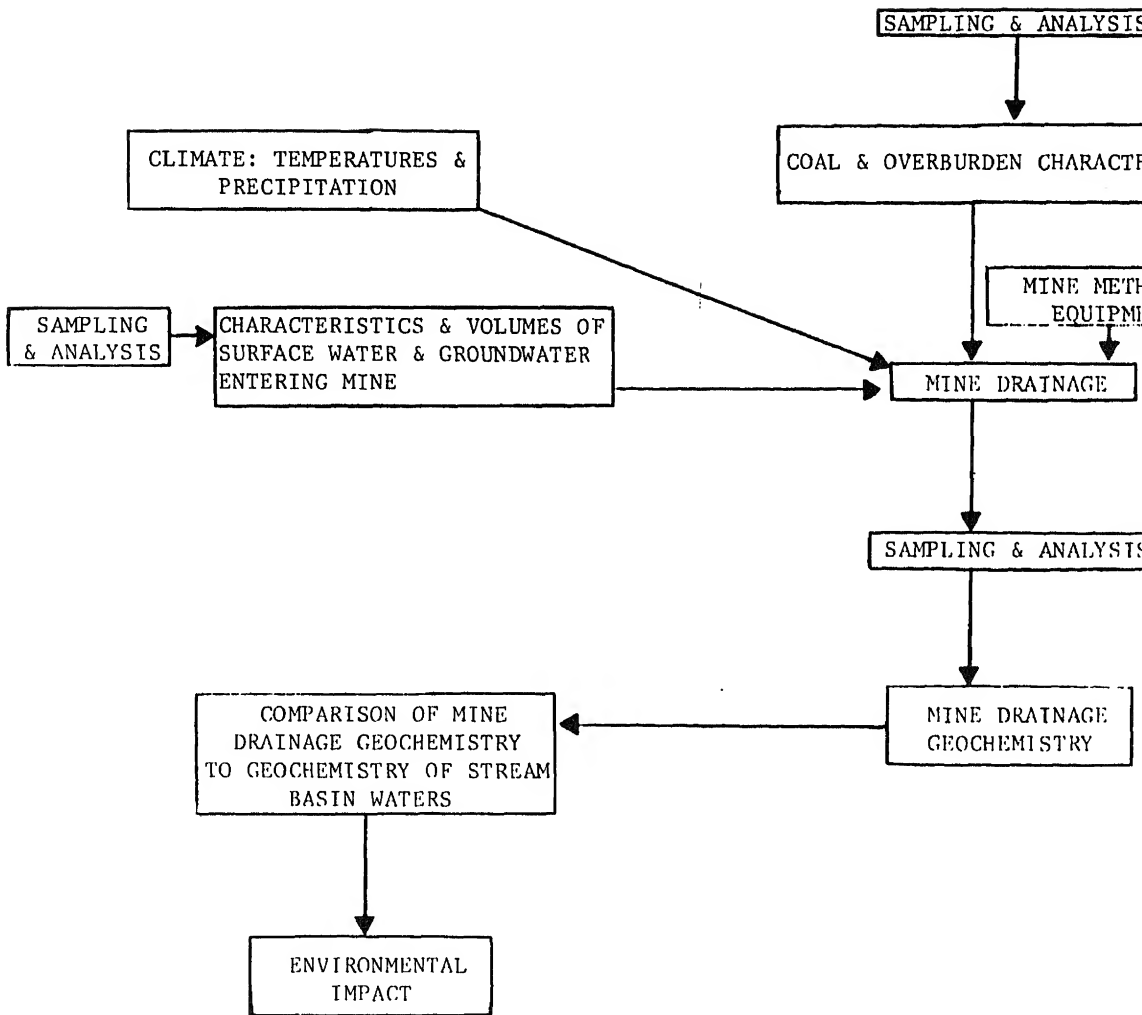
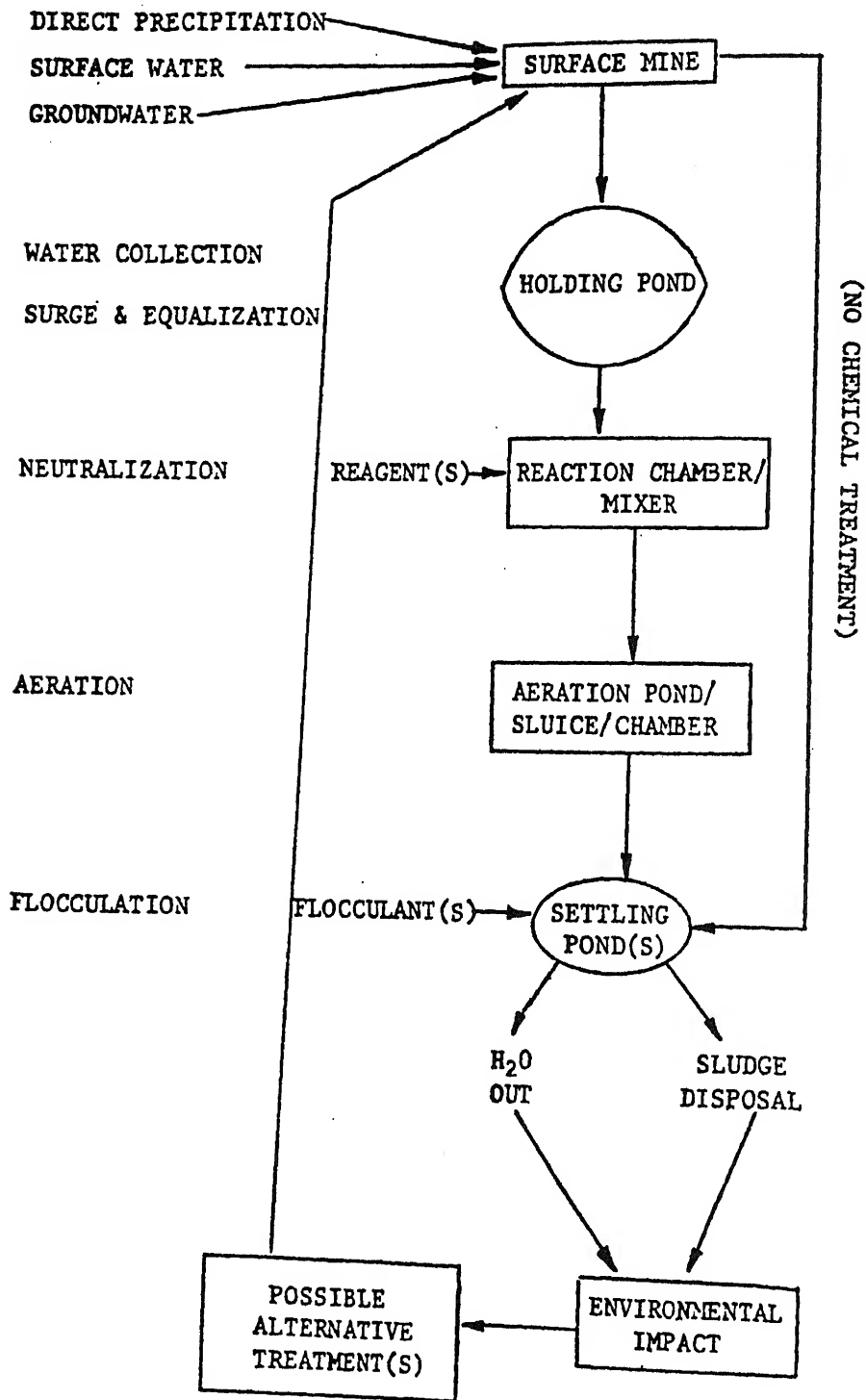


Fig. 2. Subunit Operations: Mine Drainage Geochemistry (Task 2)





Other data bank storage and retrieval systems. Input data include chemical analyses of surface water, coal, and overburden, as well as background information on sites and methods of sampling and analysis.

#### TASK 4 - EFFLUENT LIMITATIONS GUIDELINES

The mine effluent analytical data gathered under Task 2 are being examined in relation to EPA's recently established effluent limitations guidelines and new source performance standards for the coal mining point source category. These standards and effluent limitations have been incorporated into the Office of Surface Mining Reclamation and Enforcement's proposed rules for a permanent regulatory program. The applicability of guidelines and standards on a national scale versus state or regional scale will be analyzed. The data from this program will be used to assess the validity of the guidelines in general and in relation to current and future technology. Recommendations for modifying or implementing the guidelines will be developed. Figure 4 shows the operations which will be utilized in Task 4.

#### TASK 5 - SUMMARY REPORT

Argonne National Laboratory will write a summary report integrating chemical data from the various sites with a discussion of generic environmental control problems, the pollution control technology involved, and the control technology effectiveness. Included in this final report will be recommendations for environmentally effective control technology for new mine openings, and alternate control technologies for existing and expanding mines. Recommendations will also be made for research on advanced control technologies based on criteria and needs determined by this project.

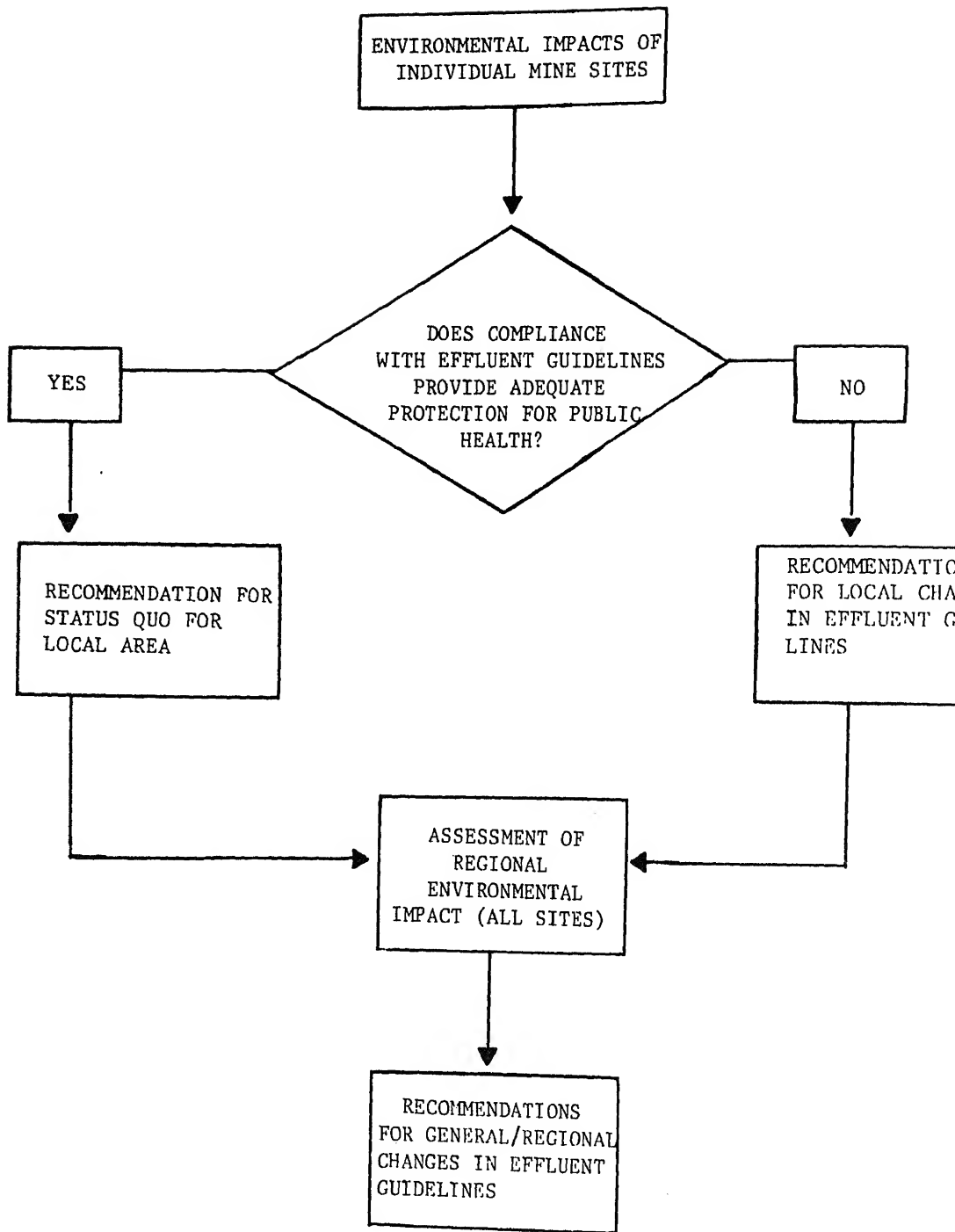
### RESULTS

Two examples of program output -- control technology efficiency and treatment costs -- are described in this report:

#### CONTROL TECHNOLOGY EFFICIENCY

##### Mine PA-1

Two mines in Pennsylvania, PA-1 and PA-3, serve as examples of adequate and inadequate treatment. At mine PA-1, water from an active mine is pumped through a six-inch flexible vinyl hose for several hundred yards to a flash mixer powered by the water velocity from the pump. The mixer is housed in a small wooden shed. Approximately 50 pounds of hydrated lime is manually added to the mixer every two hours. The mixer effluent flows through a wooden sluice box into the first of three settling ponds. Most of the sludge and sediment is retained in the first pond; retention time for this pond is estimated to be approximately nine hours.



allowable maximum standards for suspended solids and manganese, indicating treatment was necessary. Values for pit water pH were in violation of the allowable maximum standards in three out of twenty-six sampling visits; iron values were in violation twice during the sampling period.

Following treatment, data from the first settling pond outflow (B) indicate compliance (maximum allowable) was attained for the mean of all four parameters, although occasionally levels of suspended solids (three out of 23 visits) and manganese (three out of 22 visits) were in violation of the standards.

Data from the second settling pond outflow (C) show a lesser incidence of violating the maximum allowable standards.

In general, the effluent discharged from this site met the maximum allowable effluent limitations. The lime treatment was adequate and effective. There were occasions when pH, manganese, and suspended solids levels were not in compliance, a situation reflecting inadequate process controls since the operation is manually operated and controlled.

### Mine PA-3

Water treatment at mine PA-3 consists of collecting pit water in a sump; adding an alkali reagent occasionally, but not necessarily regularly, then pumping the effluent into the first of three settling ponds. The soda ash ( $\text{Na}_2\text{CO}_3$ ), is mixed by hand with pumped pit water in a 55-gallon drum that is perforated in its lower portion and base to allow the dissolved reagent to flow back into the sump. The water pumped into the settling pond had minimal retention time as the ponds were nearly filled with solids, coal fines. A secondary treatment, only occasionally used, consisted of a perforated bucket filled with soda ash briquettes or hydrated lime below the outflow of the first settling pond.

The values listed in Table 3 show the pit water (mean values for suspended solids, manganese, and iron and the range of values for pH) in violation of the maximum allowable standards for each of the four parameters. Following treatment some improvement was noted in all four parameters, but the values (B) still show the mine is not in compliance. Only once during the entire range of sampling dates was the pH raised to an acceptable level, but on this date the suspended solids reached 1800 mg/L indicating only partial treatment, poor settling sludge characteristics, and probably inadequate retention time. Iron levels in the first pond were in compliance on less than half of the sampling dates, suspended solids 60% of the time, and manganese only 10% of the time.

Effluent from the final settling pond outflow (C) was in compliance only for mean values for suspended solids; although minimal improvement was noted, mean values for pH, iron, and manganese were still in violation of the guidelines. For the final effluent leaving the mining site, violations of standards for suspended solids occurred on 20% of the sampling dates,

Table 1. Effluent Limitations  
per Liter (mg/L) except for pH

Effluent	Maximum Allowable	Average of daily values for 30 consecutive discharge days
pH <sup>a</sup>	Within range of 6.0 - 9.0	
Total suspended solids <sup>b</sup>	70.0	35.0
Iron, total	7.0	3.5
Manganese, total <sup>c</sup>	4.0	2.0

<sup>a</sup> Where the application of neutralization and sedimentation treatment technology results in inability to comply with the manganese limitations set forth, the regulatory authority may allow the pH level in the discharge to exceed to a small extent the upper limit of 9.0 in order that the manganese limitations will be achieved.

<sup>b</sup> Limitations given are for eastern and midwestern states. Western states are treated on a case-by-case basis, but levels must not be greater than 45 mg/L (maximum allowable) and 30 mg/L (average of daily values for 30 consecutive discharge days) based on a representative sampling.

<sup>c</sup> The manganese limitations shall not apply to untreated discharges which are alkaline as defined by the EPA (40 CFR 434).

Effluent	Standard	Mean	Min.	Max.
pH	6 - 9		3.6 6.3 4.2	7.1 8.8 8.7
Total suspended solids	70 mg/L	A. 162.4 B. 39.3 C. 14.6	14.0 4.0 0.0	1380.0 203.0 124.0
Total iron	7.0 mg/L	A. 4.1 B. 1.0 C. 0.5	0.0 0.0 0.0	14.0 3.8 2.8
Total manganese	4.0 mg/L	A. 5.3 B. 2.4 C. 1.7	1.2 0.5 0.2	29.2 4.2 3.7

Note: A. Pit water, 26 samples.  
 B. First pond outflow, 23 samples (Note: 22 samples for manganese).  
 C. Final pond outflow, 26 samples.

Table 3. Mine PA-3 (Units in mg/L except pH)

Effluent	Standard	Mean	Min.	Max.
pH			3.2 3.5 2.9	5.9 8.5 6.7
Total suspended solids	70 mg/L	A. 185.6 B. 2544.6 C. 58.7	0.7 5.0 3.0	2600.0 43350.0 380.0
Total iron	7.0 mg/L	A. 21.2 B. 16.9 C. 12.8	2.6 0.1 0.1	110.0 94.0 41.3
Total manganese	4.0 mg/L	A. 12.0 B. 15.3 C. 15.1	1.1 1.5 3.1	27.0 28.0 27.0

Note: A. Pit water, 24 samples.  
 B. First pond outflow, 18 samples.  
 C. Final pond outflow, 24 samples.

In contrast to mine PA-1, effluent discharged from mine PA-3 rarely met the effluent guidelines. The soda ash treatment was erratic, total suspended solids uncontrolled, and inadequate. The sedimentation ponds were nearly filled with solids and channels developed which allowed the water to pass rapidly through the ponds, resulting in negligible retention time for flocculation and settling of solids. Often the suspended solids concentration increased between the pit water and the final settling pond.

#### TREATMENT COST FOR MINE PA-1

Since mine PA-1 is conscientiously attempting to comply with the effluent limitations guidelines, an examination of its most recent treatment cost data gives an indication of the level of costs that the industry faces in maintaining compliance.

Mine PA-1's operation ultimately will affect 100 acres, 95 of which contain coal. The average coal thickness is 3'1" and, at the standard rate of 1800 tons/acre ft of coal, each acre contains approximately 5600 tons of coal. At a recovery rate of 90% for surface mined coal, this mine will produce 478,800 tons of coal (95 acres x 5600 tons/acre x 0.9 [recovery rate] = 478,800 tons).

In order to control the sediment related to the mining, storage and diversion ditches need to be constructed and, after mining ceases, reclaimed. The sediment collected in these ponds during the mining operation must also be removed and handled in a manner consistent with environmental standards. The following costs and assumptions were based on discussions with on-site company personnel. These costs are life-of-mine costs and are related to the total tonnage the mine is expected to produce.

#### Sediment Control

##### 1. Pond Construction

Sediment storage:  $0.2 \text{ acre ft/acre of disturbance} \times 100 \text{ acres disturbed} = 20 \text{ acre ft.}$

Storm water storage (10 yr - 24 hour storm):  $4" \text{ rainfall} \times 0.4 \text{ (runoff coefficient)} \times 100 = 17 \text{ acre ft.}$

Total capacity needed = 37 acre ft.

Plan: 3 ponds, 12-15 acre ft. each.

Cost per pond:

Earthwork and seeding	\$ 8,000
Discharge pipe	\$ 1,500

## 2. Sediment and Pond Removal

Sediment removal: Assume 10 acre ft (16,100 cu yd of sediment)  
Removal and disposal @ \$2.50 cu yd = \$40,250

Pond removal = 1/2 of construction cost = \$20,500.

## 3. Diversion Ditches

9000 ft @ \$2.50/ft = \$22,500.

Removal = 1/2 of construction cost = \$11,250.

Total = \$33,750.

Note: 6500 ft of ditch built under old law specifications exists. Estimated cost of that ditch, 6500 ft x \$1.50/ft = \$9,750. New cost under new law = \$24,000.

## Summary of Sediment Control Costs

Pond construction	\$ 40,500
Sediment and pond removal	\$ 60,750
Diversion ditches	\$ 24,000
	<hr/>
Total cost	\$125,250
Cost/ton - \$125,250/478,800	= \$0.26/ton.

The water treatment costs were provided by the company following its investigation of compliance costs for a recent six-month period in 1971 to meet the new effluent limitations. The mine has complied with most effluent discharge criteria except for periodic violations of the manganese limitation. Production was 65,000 tons for the six-month period.

## Water Treatment Cost - Six-Month Period

### Equipment and Power

Pumps, hoses, and misc.	\$650/month	\$ 3,900
Electric and fuel	\$350/month	\$ 2,100
Lime (100 tons)	\$ 55/ton	\$ 5,500

### Ponds

3 @ 1.8 acre ft each pond	\$ 1,800 each
Earthwork	\$ 1,200 each
	<hr/>
Seedling, mulching, misc.	\$ 3,000 each

Engineering and Management

15% of equipment and labor

\$21,700

Summary of Water Treatment Costs (Six Months)

Equipment and Power	\$ 6,000
Lime	\$ 5,500
Ponds	\$ 9,000
Equipment and Labor	\$124,450
Engineering and Management	\$ 21,700

Total \$166,650

Cost/ton =  $\$166,650 / 65,000 =$  \$2.56/ton

Total sediment control and water treatment cost = \$2.82/ton.

The total cost of \$2.82/ton is relatively low compared to costs at our other eastern sites because the affected area of the mine has rather shallow slopes. As the slope angle increases, our preliminary findings indicate a corresponding rapid increase in sediment control costs, with final costs often exceeding \$7/ton. The costs presented for mine PA-1 still do not represent costs for total compliance, as the manganese standard is often violated. The company estimated an additional \$0.65-\$0.75/ton for full compliance.

#### CONCLUSIONS ON CONTROL TECHNOLOGY EFFECTIVENESS

The major conclusion drawn from this survey of control technology at sites PA-1 and PA-3 and at other surface mines is that the ECT "state-of-the-art" is generally at a very low level. Related conclusions include:

1. At the present time, mine drainage control and treatment at surface coal mines may not reflect conscientious planning and engineering design work by mine operators. On the whole, control technology (including reagent application) may be haphazard and periodically inefficient. However, there are some notable exceptions.
2. Surface mine operators favor small, efficient, and above all, portable application systems for neutralization reagents. Because effluent discharge points at surface coal mines do not remain constant over long periods of time and because discharges are generally small (< 5 gpm) and variable, it is



3. When choosing a reagent to neutralize mine drainage, reagent cost per unit quantity is less of a deciding factor to surface coal mine operators than ease of reagent application and handling. Thus, small caustic soda (NaOH) and soda ash (Na<sub>2</sub>CO<sub>3</sub>) treatment systems are common, even though reagent costs (based on treating water of equivalent acidity) may be several times the cost of hydrated lime or limestone treatment.
4. There needs to be more pre-mining planning by surface mine operators to develop mining methodologies which minimize pyrite oxidation and hydration. Some additional investment in exploration plus a prudent choice of a mine plan, drainage plan, and reclamation plan may minimize the generation of poor quality effluents. Mine operators may thus realize economic benefits from minimal initial investments which prevent the generation of poor quality effluents, as opposed to the operators' maintaining treatment facilities during and after mining, a long and costly process.
5. Costs for compliance with EPA/OSM effluent limitations can range from \$3-\$7/ton. The higher costs are associated with steeply-sloped terrain.

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## 1. INTRODUCTION

Coal from mines is transported to its ultimate destination by rail, barge or pipeline. Once it arrives at its consumption point or a processing facility, it is moved over short distances by rubber-tired loaders, conveyor or rail shuttle cars. During the transportation process, the coal is exposed to the elements. This leads to dust emissions and losses through effects. Moisture absorption and oxidation also can occur, causing deterioration of the coal and loss in fuel value (ERDA, 1976).

Once at the destination, the coal is either used or stored. Most users maintain stockpiles comprising a 90-day supply at their normal use rate. This is done primarily to provide a reserve in the event of temporary loss of supply. This stockpile may stand for a year or more before it is necessary to use it.

In the stockpile, the coal is subject to weathering and oxidation. Dust emissions from stockpiles are common. Absorbed moisture from rain causes leachate formation and may decrease the fuel value of the coal by 1-8% depending upon initial moisture level and coal rank. Wind and rain results in coal migration and exposes new coal surface to weather. Moisture can also freeze solid in cold weather making normal handling impossible. Oxidation may reduce the heating value up to 5% over a one-year storage period (ERDA, 1976). In addition, internal oxidation can lead to spontaneous combustion in low rank fuels (ERDA, 1975; Paulson, et al., 1975).

This work presented here addresses the use of protective coatings on coal to resolve the environmental problems associated with transport and storage. These coatings not only reduce environmental pollution and improve handling characteristics, but can also be shown to provide dollar savings substantially greater than the costs of application.

## 2. TECHNICAL APPROACH

The overall objective of this work was to demonstrate the feasibility of economical coal coating systems. To accomplish this, the following factors were considered:

- Identification of suitable materials for coal coatings
- Development of formulations which are capable of reducing the adverse environmental effects of weathering of coal storage
- Identification of...

- Cost/benefit analysis

The first task was intended to provide information to guide the experimental development of coal coatings. The factors considered are listed below.

- Evaluation of candidate filler-binder materials
- Review of current coal protection techniques
- Application considerations
- User motivation

### Filler-Binder Materials Evaluation

A list of materials was generated which could be considered as candidates for inclusion in coal coating formulations. The candidate materials were screened to establish their characteristics with respect to:

- Cost
- Availability
- Fuel value
- Physical properties
- Environmental pollution potential

The filler materials considered included coal, paper, sawdust, bagasse, rice hulls, cottonseed hulls, and fly ash. Binder materials considered fall in two categories. The first included the materials useful for the hot-melt type of coating such as waxes and plastics. The second type of binder material included the various latex emulsions. This type of material was considered for use in filled latex coatings.

Pulverized coal and fly ash emerged as the best filler candidates. Both of these materials are available at coal user sites in sufficient quantities. They are both available at little or no cost, taking into account the credit for fuel value of coal. Neither of these materials would cause additional environmental problems upon combustion, as both are normally present in coal combustion systems. The other filler material candidates were either too costly, limited in availability or presented potential environmental problems. The best binder materials identified were slack wax, polyethylene, atactic polypropylene for the hot-melt composition, and polyvinyl acetate copolymers for the filled latex formulations.

### Current Coal Protection Techniques

The most common current means of protecting coal is to carefully build up and compact the stockpile, then monitor it for hot spots. At this time, it is estimated that less than 5% of the users of coal provide additional protection in the form of coatings. Coal is shipped by rail car in as-dumped condition. It is estimated that 5-10% of the shippers use latex crusting compounds to prevent wind loss and dust emissions in transit. A discussion of these current protection methods is provided below.

### Stockpile Formation

required.

Stockpiles must be properly constructed; otherwise, the risk of spontaneous combustion is high. Coal stores have been known to ignite spontaneously within six days after pile formation (Wilson, 1975). A typical method of constructing a coal stockpile is given below.

1. The coal is dumped from the rail cars either by bottom hopper or by conveyor invention.
2. The coal falls onto a conveyor and passes through a mill where it is broken down to <2-inch size pieces.
3. The coal is transported to the stockpile areas either by conveyor or by rubber-tired vehicle.
4. A bulldozer spreads the coal and compacts it. Typical piles are in the form of a truncated cone, 100-200 feet wide at the base and 25-50 feet high. The length of the pile may be up to thousands of feet.

Coal as dumped has a bulk density of about  $50 \text{ lb/ft}^3$ . After compaction the bulk density is about  $65 \text{ lb/ft}^3$  (Paulson, et al., 1975).

The stockpiling technique varies with coal source and rank. Higher rank coal may be formed into larger piles of greater height and stored longer than low rank coals (ERDA, 1975). East coast coals may be stored longer than west coast coals as they are less reactive. The finer the coal, the more reactive it is as a result of greater surface area.

Small coal stockpiles may be stored as dumped for short periods. Coal piles should not exceed 15 feet in height (Wilson, 1975). Longer term storage of uncompacted coal is risky in terms of spontaneous combustion danger. Uncompacted coal piles should be used within a few days of dumping.

### Stockpile Protection

Stockpiles are formed solely by the action of a bulldozer in shaping and compacting the pile. Thermal probes are sometimes buried in the coal to monitor pile temperatures. The probes set off an alarm if the pile temperature reaches  $130\text{--}140^\circ\text{F}$  ( $54\text{--}60^\circ\text{C}$ ).

Dust emissions from coal stockpiles are a problem of increasing concern. Some users reduce dust formation by washing the coal before piling and transporting it wet. Other users wet the pile after formation or spray it with water to reduce dust emissions.

Leachate formation is also a serious problem except in the case of high grade coal. Water runoff from the pile is collected in a trough around the pile. It is then sent to a holding tank or pond where it is treated before discharge to the environment. The treatment generally consists of adding a flocculant or precipitating agent, then allowing the solids to settle out.

in the first year of storage. Leonard (1968) found that properly stored coal will lose only 1-2% per year of its energy value due to oxidation. However, improper storage was found to result in losses of 3-5% per year.

### Latex Crusting Compounds

The only protective coating of significance in current use is the latex crusting compound. This material is essentially a paint base, and it is produced by paint manufacturers. Numerous small firms purchase this material and resell it as a protective coating for coal or as a surface stabilizer for earth, sand or other materials stored in stockpiles. The latex compounds are normally applied after dilution by a factor of 3/1 to 20/1. They are sprayed onto the material to be protected using any equipment capable of spraying.

### Formulation and Evaluation of Coatings

During this work, 119 hot-melt formulations and 39 latex mixes were produced and evaluated. The types of tests conducted were as follows:

Visual observation	Viscosity
cracking tendency	Density
surface texture	Thermal expansion
adhesion to substrate	Water permeability
Compressive strength	Rheology
Tensile strength	Grindability

Not all tests were run on all formulations. Some tests, such as tensile and compressive strength, were run on a limited number of specimens to establish the order of magnitude of the results. No means of converting strength data into a useful parameter for characterizing the utility of coatings was identified. Thus, the data are of interest primarily as a means of estimating cracking potential.

Other tests, such as water permeability, effects of thermal cycling and efficiency of thermal expansion relate directly to the quality of the coating. Tables I and II summarize the results of these tests on formulations that are near the optimum compositions for both the hot-melt and filled latex coatings.

### Test Panels

Those formulations which appeared to best meet the above criteria were cast onto frames, 12" x 12", with about 3-4" of coal as a substrate. The frames were constructed with wooden pegs spaced at 3/4" intervals around the periphery. The pegs served to restrain the coating from shrinkage to enhance crack formation and present a more realistic test than would an unrestrained coating. The coating was applied in thicknesses ranging from 1/8" to 1/2". Figure 1 shows two views of a test frame with a hot-melt coating in place. Figure 2 shows a cross-section view of the coating on a coal bed.

The test frames were subjected to a "rainfall" test. In this test,

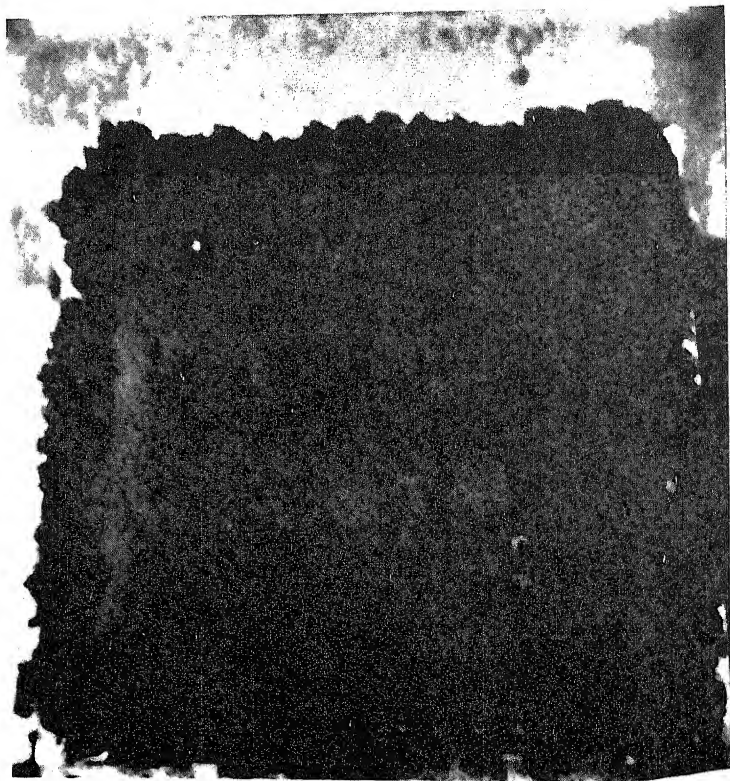
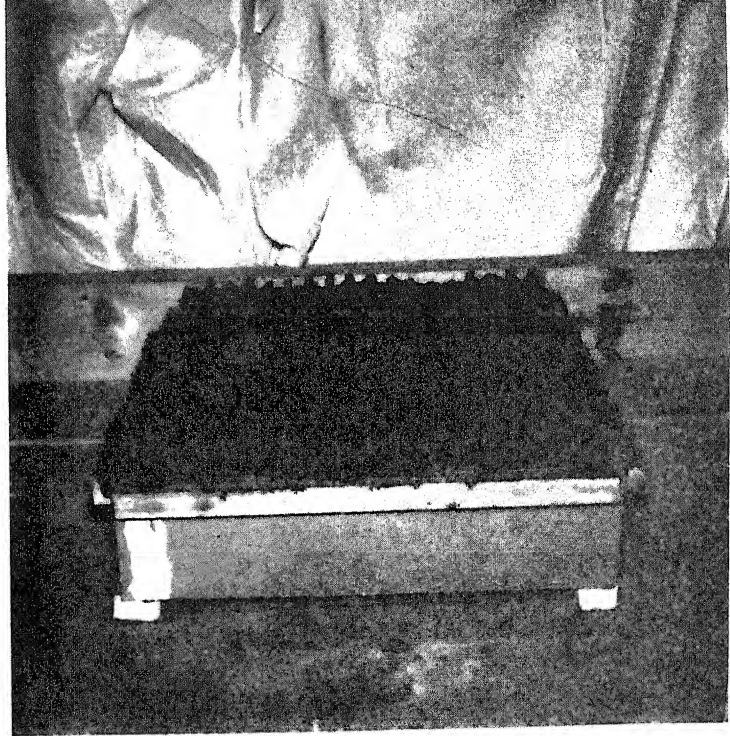
Table I. Physical Properties of Hot-Melt Formulations

NO.	COMPOSITION	VISCOSITY			TENSILE PROPERTIES		TENSILE PROPERTIES (-30°F)		COMPRESSIVE STRENGTH, (70°F) at Failure (PSI)	STRAIN IN COMPRESSION At Failure (%)	DENSITY GM/cm <sup>3</sup> (70°F)
		Avg. Kp	1	2.5	5	At Rupture	Stress (PSI)	Strain (%)	Tangent Modulus (PSI)		
-4	85.0% Coal 12.0% SW 3.0% PE										
							333			1.9	
							392		Avg 342	1.3	
							302			1.6	
-1	85.0% Coal 12.0% SW 3.0% PE						248			1.8	
							278		Avg 258	2.1	
							249			2.1	
-2	85.0% Coal 12.0% SW 3.0% PE						148			2.2	
							179		Avg 173	1.9	
							192			2.3	
3	77.5% Coal 14.9% SW 3.8% PP 3.8% PE		8	7	4	210 79		0.4 0.7	106,000 18,200		1.1
2	80.0% Coal 15.2% SW 2.4% PP 2.4% PE					222 233 241		0.4 0.6 0.5	84,800 68,200 83,600		1.08

Slack Wax  
Polyethylene  
Polypropylene

Table II. Characteristics of Hot-Melt and Filled Latex Compositions

RECEIVED NUMBERS	LEAK RATE, % OF SPRAY		36" Shrinkage	CTE STRIP		AVERAGE CTE	RESTRAINED ENDS GAP	GRINDABILITY
	70°F	+160°F		Reheat	Shrinkage			
2								
80.0% Coal								
13.4% SW								
3.3% PE	3.3	8.1	11.0	-	0.335"	$7.6 \times 10^{-5}$	-	Fair
3.3% PP								
3								
77.5% Coal								
14.9% SW								
3.8% PE	1.4	5.2	8.0	-	0.305"	$6.6 \times 10^{-5}$	-	Fair
3.8% PP								
2, 5-30-1								
80.0% Coal								
15.2% SW								
2.4% PE	14.0	20.0	78.0	0.278"	0.285"	$6.2 \times 10^{-5}$	0.118"	Fair
2.4% PP								
50.0% Coal								
23.0% Vinyl acetate copolymer	7.7	1.8	1.2					Good
27.0% Water								
Slack Wax								
Polyethylene								
Polypropylene								







Thermal expansion or contraction is an important characteristic of melt coatings. If the degree of contraction upon cooling exceeds the strain-to-failure of a coating material, cracking will result. Similarly, if the thermal expansion upon heating exceeds the compressive strain-to-failure of the coating, the coating will shatter.

The coatings listed exhibited Coefficients of Thermal Expansion (CTE) ranging from  $6 \times 10^{-5}$  to  $14 \times 10^{-5}$  in/in°F. Thus, for a 100°F temperature change, the degree of expansion or contraction would be about 0.6% to 1.4%. The tensile strain to failure was measured to be about 0.5%. Thus, most coatings would be expected to crack upon cooling by 100°F or more. Heating would not appear to be a problem. Compressive strain-to-failure was measured to be about 2%, and none of the coatings tested expanded that much.

The CTE is not the only factor in cracking of the hot-melt coatings. The materials were generally cast at 200-250°F. In general, the coatings remained fluid until they cooled to below 200°F. They then start to shrink, if unconstrained. Total shrinkage upon cooling to 70°F ranged from 0.6% to 1.7%. Cooling behavior was a function of the composition, however. The CTE values for typical compositions are shown in Figures 3 and 4. Formulations with values similar to that shown in Figure 4 would probably be satisfactory for stockpile applications.

#### Latex Formulation Results

A total of 39 latex formulations were prepared and evaluated during this work. Included in this number were four tests of commercially available crusting compounds for comparison purposes. The remainder of the formulations were filled latexes, in which pulverized coal was used as an extender to prove the waterproofing character of the latexes.

Some of the latexes tested were not compatible with coal. In the presence of coal, they coagulated or solidified rapidly. Daratak SP-1065, Everflex and DLR-H resins yielded satisfactory coating films. All others tested were incompatible with the coal.

The probable reason for the observed incompatibility is de-emulsification of the resin by chemical reaction with ionic components of the coal. Another possibility is instability resulting from pH change because of acidic substances in the coal.

Filled latex coatings made with polyvinyl acetate resins were applied to 1-ft x 1-ft panels similar to those previously described for the hot-melt coatings. All of the coatings were leakers in the "rainfall" test. The best of these coatings was an Everflex GT mix with 50% coal, which exhibited only a 13% leak rate.

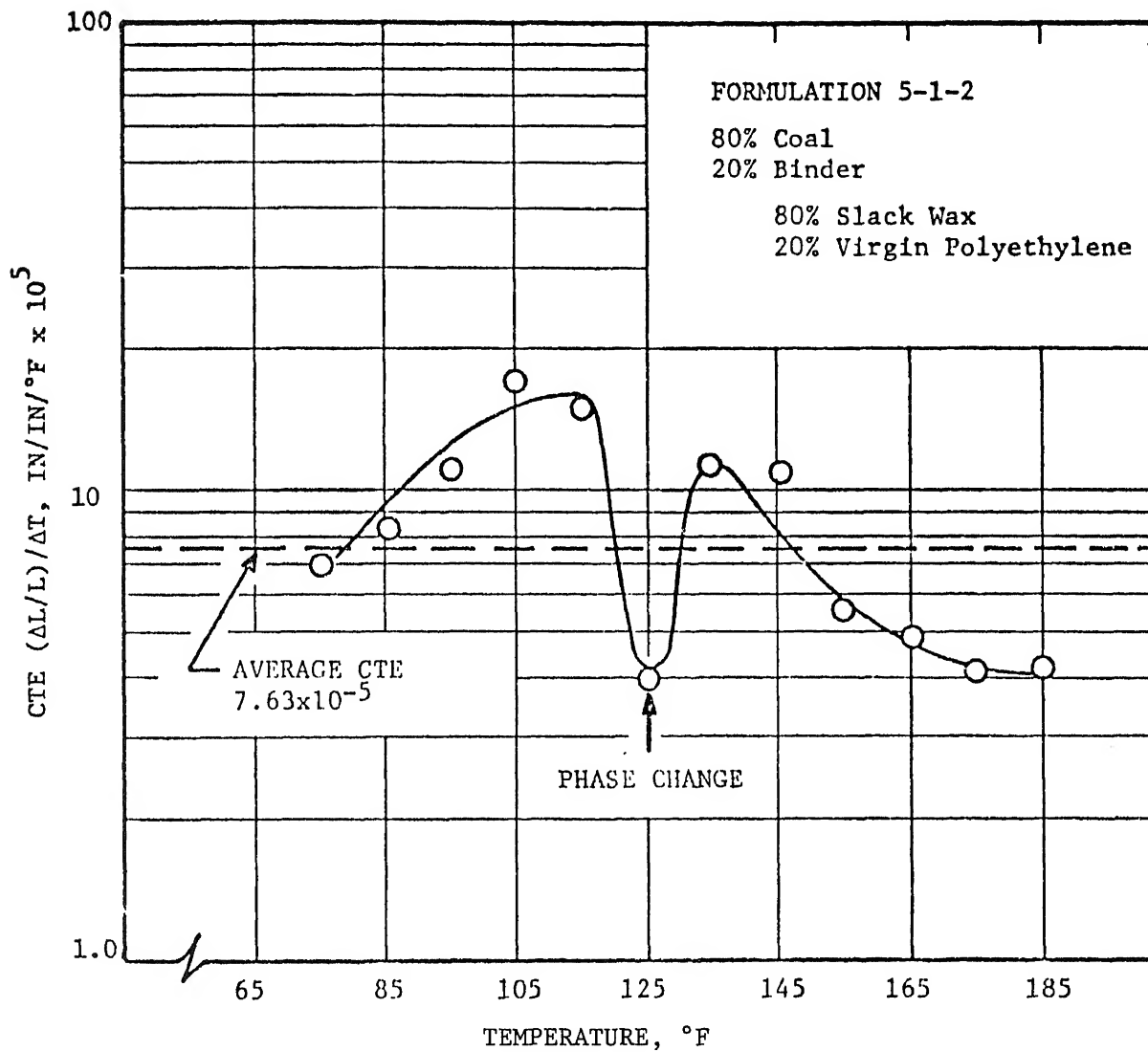


Figure 3. Coefficient of Thermal Expansion Curve for Formulation 5-1-2

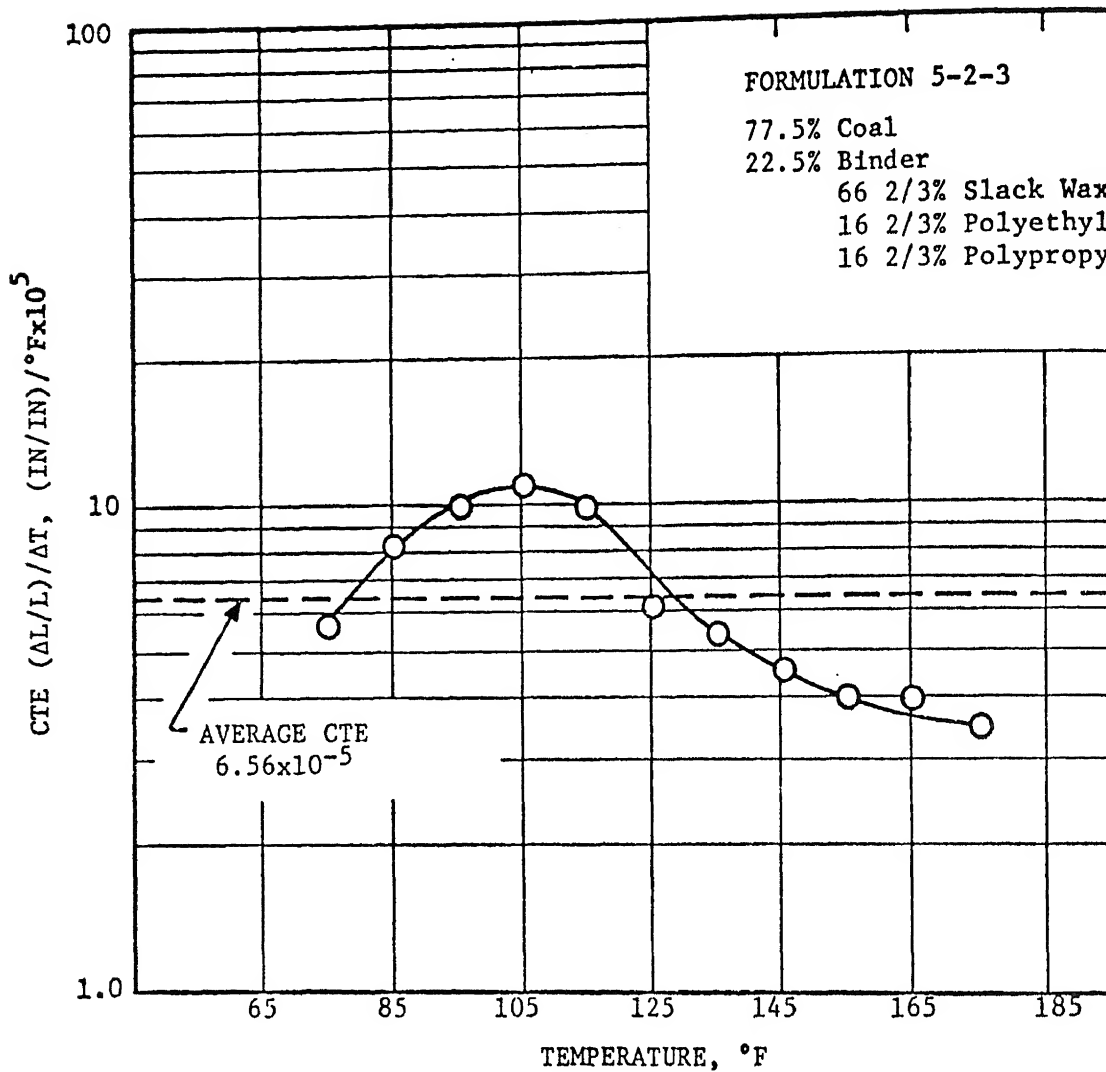


Figure 4. Coefficient of Thermal Expansion Curve for Formulation 5

coating did form a cohesive film on the surface, however. Less than 8% of the "rainfall" water adhered to the surface or passed through the coating even after exposure to a temperature range of  $-30^{\circ}\text{F}$  to  $+160^{\circ}\text{F}$ . In the economic analysis, presented later in this paper, filled latex coatings on both normal and specially prepared surfaces are considered for comparison purposes.

Tests on commercial latex crusting compounds showed that they do not provide a significant degree of waterproofing to coal. The minimum leak rate noted was 78%. One commercial product was tested at the recommended concentration and again at 5 times the recommended amount. The leakage rate was similar in both cases. The unfilled latexes cannot be considered as a satisfactory waterproofing agent for coal stores even when applied at substantially higher levels than recommended by the manufacturers for dust control and face stabilization.

### Application Techniques

Application experiments were conducted to assess characteristics of melt materials. The principal objective was to assure that the materials could be pumped without problems due to viscous effects or vapor lock. Initial experiments showed that compositions containing 80% coal were easily transported through a one-inch diameter tube. Flow was initiated with less than 2 psig pressure differential.

A system capable of applying hot-melt materials comprises the following elements:

- |                           |                           |
|---------------------------|---------------------------|
| a) Crusher/grinder        | f) Slurry pump (heated)   |
| b) Polymer melt vessel    | g) Service lines (heated) |
| c) Coal preheater         | h) Steam boiler           |
| d) Metering system        | i) Dispensing system      |
| e) Mixing vessel (heated) |                           |

A schematic of the system is shown in Figure 5. As shown, a mixing vessel is included in the current subscale apparatus. This mixer is used as a batch heater and dispenser. For larger-scale applications, a continuous system would be more desirable.

Hot flow application resulted in an excellent layer of coating on an inclined 4 x 8 foot panel. The material thickness varied from 1/8 to 1/4 inch thick. Figure 6 shows a technician in the process of coating a 4x8 foot panel.

## 3. ECONOMIC ANALYSIS

The following section is an evaluation of the costs and benefits which would accrue from the use of protective coatings for coal. Uses of latex crusting compounds, filled latex coating and hot-melt coatings are considered.

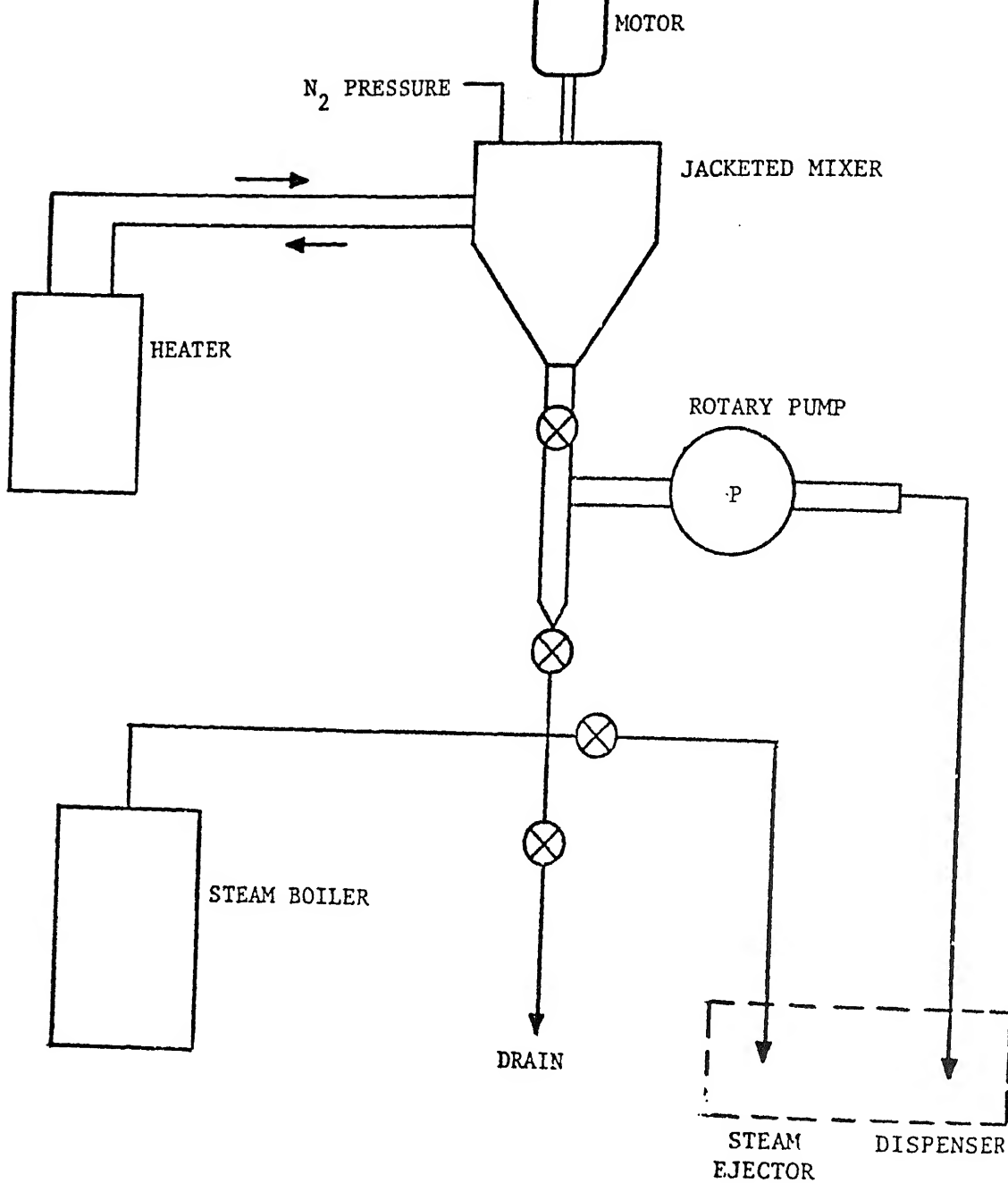


Figure 5. Schematic Diagram: Coal Cover Application System



Figure 6. Application of Hot-Melt Coatings

Dump coal from cars  
Grind to <2 inches  
Transport to pile  
Unload on pile  
Form and compact pile

Current practice, unprotected pile

<u>Latex Crust</u>	<u>Filled Latex</u>	<u>Hot Melt</u>
1. Mix with water, 3-10/1	1. Grind coal for surface preparation*	1. Grind coal for coating mix
2. Spray apply 4-11 gal/500 ft <sup>2</sup>	2. Grind coal for coating mix	2. Prepare wax/pl. binder
	3. Mix coal, water, latex	3. Heat and mix components
	4. Spray apply 7-31 gal/500 ft <sup>2</sup>	4. Spray apply 20- gal/500 ft <sup>2</sup>

\* optional

#### Summary of Stockpile and Rail Car Protection Costs

Table IV shows a summary of the costs of building and protecting a coal stockpile. A 250,000 ton stockpile was used as a basis for comparison. Table V is a summary of the costs of various techniques for protecting coal in rail cars.

Table IV. Summary of Stockpile Protection Costs  
Basis: 250,000 ton stockpile

<u>Treatment</u>	<u>Time Required</u> <u>Days</u>	<u>Total Cost</u> <u>\$</u>	<u>Cost/</u> <u>\$</u>
Build and Compact Stockpile	50	55,000	0.2
Monitor Stockpile for 1 year	365	22,750	0.0
Latex Crusting Compound, 1 gal/200 ft <sup>2</sup>	3.5	8,400	0.0
Filled Latex on Surface Fines, .025"	13.3	19,500	0.0
Filled Latex on Surface Fines, .050"	26.6	25,908	0.1
Filled Latex on Surface Fines, .100"	53.2	42,000	0.1
Filled Latex on Normal Surface, 1/8"	11.7	33,506	0.1
Hot-melt on Normal Surface, 1/8"	11.17	12,788	0.0
Hot-melt on Normal Surface, 1/4"	23.4	25,576	0.10



Treatment	Total Cost \$	Cost/Ton \$
Latex Crusting Compound, 1 gal/500 ft <sup>2</sup>	700	0.07
Filled Latex on Surface Fines, .050"	3,844	0.38
Filled Latex on as Dumped Surface, 1/8"	4,320	0.43
Holt-melt on as Dumped Surface, 1/8"	1,355	0.14

### Cost/Benefit Analysis - Stockpile Applications

This section illustrates the benefits to be derived from coal protection and the estimated return on investment. This analysis is based upon protection of a 250,000 ton stockpile for a period of one year. The value of the coal is assumed to be \$20 per ton.

The cost factors used in determining treatment costs are listed below.

	Cost, \$/Ton
Build and compact pile	0.08
Apply latex crusting compound	0.034
Apply filled latex coating, 0.025"	0.087
Apply hot-melt coating, 1/8"	0.051

The benefit factors used in determining the return on cost of applying particular coatings are:

- Reduce or eliminate dust emissions.
- Reduce or eliminate leachate formation.
- Maintain or reduce moisture content (fuel value effect).
- Minimize freezing of coal into large agglomerates.
- Prevent increase in moisture content (grinder operation).
- Prevent stockpile migration.
- Reduce or eliminate oxidative energy loss.
- Reduce or eliminate spontaneous ignition.
- Prevent wind or rain erosion.
- Reduce need for snow removal.
- Reduce monitoring costs.
- Reduce fire prevention and extinguishment requirements.

The basis for determining the dollar value or equivalent for these benefit factors is described in Kromrey, et al., (1978). The results are summarized below. From this summary, the highest return per unit cost occurs by using the hot-melt formulation, i.e., return of benefits valued at \$1.90 per ton at a cost of 13.1¢ per ton.

Filled Latex Coating*	0.158	1.04	1.63
Hot-melt Coating*	0.131	1.04	1.90

\* includes compaction

### Cost/Benefit Analysis - Rail Car Applications

This section illustrates the benefits to be derived for protection of coal in rail cars and the estimated return on investment. The results are based upon protection of a unit of 100 cars containing 100 tons each of coal. The value of the coal is assumed to be \$20 per ton. The benefit factors considered are listed below:

- Reduce or eliminate dust emission.
- Reduce wind losses.
- Prevent moisture increase (fuel value effect).
- Prevent moisture increase (grinder operation).
- Prevent freezing of coal into large agglomerates.
- Reduce or eliminate spontaneous combustion.

Again, the basis used to convert these factors into an equivalent dollar value is described in Kromrey, et al. (1978). The results are summarized below. This summary indicates the benefit return per unit cost to be had for the latex crusting compounds with \$.74 per ton in benefit value resulting from costs of \$.07 per ton. For rail car applications, the latex crusting appears to be most cost-effective.

Treatment	Treatment Costs, \$/ton	Direct \$ Savings, \$/ton	Total Benefit Value, Equivalent \$/ton
Latex Crust	0.07	0.54	0.74
Filled Latex Coating	0.38	0.61	0.81
Hot-melt Coating	0.14	0.61	1.01

### 4. CONCLUSIONS

Based upon the results of this technical effort, the following conclusions are presented:

1. Commercially available latex resins used as coal crusting compounds can prevent dust loss and wind erosion, but do not waterproof the coal surface.
2. Hot-melt formulations consisting of about 77.5% coal, 15% slack wax, 3.75% polyethylene and 3.75% polypropylene are capable of sealing a coal surface against water penetration.

water penetration provided the surface is coated with fines of less than about 1/8" particle size.

4. Hot-melt coatings appear to be most cost effective for application to coal stockpiles.
5. Latex crusting compounds appear to be the most cost effective means of protecting coal in rail cars.
6. The anticipated return in dollars and intangible benefits by use of the coal protection methods described herein is in the range of 10-15 times the cost of such protection.

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## ABSTRACT

Enhanced oil-recovery processes are still developing. The transition from pilot testing to full-scale field application depends upon the success of field research that may improve the economy of enhanced oil-recovery processes. Underlying all development and expansion activities associated with oil production is the constant need to protect the environment from pollution. Unanswered questions regarding the environmental consequences of enhanced oil-recovery activities should be addressed during the period of pilot field testing.

Oil displacement by injection of brines (the waterflood process) entails the surface processing of large quantities of saline waters creating the potential for pollution of surface waters and shallow freshwater aquifers. Improved waterflooding techniques involve the introduction of surface active agents (detergents), caustics, and organic polymer compounds (particularly polyacrylamide), thus increasing the potential for pollution. It is increased further by the micellar-polymer process since the micellar solution is a mixture of surfactant, oil, water and a cosurfactant (usually an alcohol).

Enhancement of oil production by thermal methods adds another dimension to the environmental hazards through air pollution from steam generators and the produced fluids.

Other field operations, such as drilling and renovation of wells, create local environmental hazards, but these are becoming regional concerns as the search for new oil and the reactivation of old oilfields accelerates. This paper presents the potential pollution hazards of the enhanced oil-recovery processes and the environmental surveillance program being instituted by DOE.

## INTRODUCTION

We are safe in predicting that the future will bring with it a greater population density. To maintain our standard of living, engineering technology will have more stringent demands.

making life comfortable and healthy. However, in filling consumer needs, engineers cannot ignore the ecological considerations of every technological process. Governmental controls, economic considerations, and diminishing resources have forced complete re-evaluation of waste effluents from all industries. Waste must be negligible for the sake of the economy as well as providing safety within the environment in which we live.

Enhanced oil-recovery processes are still developing. The transition from pilot testing to full scale field application depends on the economic success of field research. Underlying all development and expansion activities associated with oil production is the constant need for protecting the environment from pollution. Unanswered questions regarding the environmental consequences of enhanced oil-recovery (EOR) activities should be addressed during the period of pilot field testing, now in progress. Environmental data can be obtained from pilot projects that discharges can be correlated over time with reservoir characteristics and process variables for use in planning field wide commercial implementation of any process.

Potential adverse environmental concerns are enhanced by injection of large quantities of chemicals to displace oil in producing wells. New chemical processes for oil recovery require surface processing of large quantities of saline waters as well as chemical mixtures. The large volumes of fluids create a potential for pollution of surface waters and shallow freshwater aquifers. When the oilfield is finally abandoned large quantities of chemicals used for oil displacement will be left in the underground reservoir, creating a potential for long-term environmental hazards.

The United States Congress and State Legislatures have enacted laws intended to protect our environment from pollution due to human endeavors. Several of these laws have a direct bearing on enhanced oil recovery, the most significant of which are the Clean Air, Federal Water Pollution Control, and Safe Drinking Water Acts.

Research with chemicals intended for use in enhanced oil recovery is the best way to avert adverse environmental effects. The Department of Energy has initiated several research projects to examine the biological and chemical degradation of EOR chemicals, the effects of injected chemicals on geologic strata, toxicity of chemicals, water availability, and the socio-economic aspects of enhanced oil recovery. This paper is a general overview of the environmental concerns of the enhanced oil-recovery

provides a detailed analysis of the environmental impacts of oil production in the United States. A Programmatic Environmental Impact Statement on the enhanced oil-recovery activities of the Department of Energy, which is now being prepared, will address specific aspects of developing technology.

Concern for the environment means that we do not wish to produce any kind of adverse effect on the air, water or soil from our activities. Therefore, the processes being used today for the production of oil, as well as the new enhanced oil-recovery methods being field tested, are discussed from the viewpoint of their potential for adversely affecting air, water and soil. It is important to emphasize that the current EOR field activities of DOE are nothing more than research experiments. The cost-shared field testing program with industry is designed to evaluate the utility, demonstrate the feasibility, and improve the techniques of the best technology presently available for production of oil remaining locked in the ground after secondary recovery. In pilot experiments, the environmental impacts are confined to widely scattered, isolated local sites. We tend to lose sight of this in considering the national concern over possible adverse environmental impacts from any activity. Although this report addresses the environmental aspects of EOR, it is a projection of the hypothesis that the demonstration experiments now under way will prove to be successful and result in large-scale commercialization of the EOR processes. By closely examining the pilot studies and looking ahead to commercial implementation, we hope to foresee any adverse impacts of EOR and alleviate them so commercialization can proceed in a timely manner.

## EOR PROCESSES AND ENVIRONMENTAL CONCERNS

### Secondary Oil Recovery

Secondary recovery (waterflood process) is conducted by injecting treated produced brines into oil-bearing strata to displace the oil to production wells. The brines are treated for removal of iron and suspended solids, and, after filtration, a small amount of sodium bisulfite is added to remove entrained oxygen. Sodium tripolyphosphate is then added to prevent scale formation in the pipes. The addition of the sodium bisulfate tripolyphosphate is a simple process and the concentrations used are so small that no environmental hazards exist from their use. The accumulation and processing of large volumes of oilfield brines does present serious potential environmental problems,

attributed to oil and gas-field brine-injection operations.

On the average, only about 30 percent of the original oil-in-place is produced by primary and secondary recovery methods. The remaining 70 percent of the oil in the ground is the target of tertiary recovery, or enhanced oil recovery, because this resource is estimated to be greater than 300 billion barrels of oil.

### Chemical Flood

The two EOR processes that employ, and are based upon, the technology developed for secondary recovery are known as Chemical Flooding (or Improved Waterflooding), and the Micellar-Polymer Process. Chemical Flooding, as the name implies, involves the addition of chemicals to the brine prior to injection. At present three types of chemical compounds are in the forefront of chemical flooding. These are caustics (sodium hydroxide, sodium silicate, ammonium hydroxide, etc), detergents (alkyl aryl sulfonates), and polymers (polyacrylamide and polysaccharide). A large body of experience has already been accumulated in the use of polymer solutions in oilfields, since more than 100 fields have been treated with polymers of various kinds.

The construction of additional facilities (mixing tanks, storage tanks, pumps, pipes, etc.) are necessary to mix and process the chemical solutions at the field site: however, the additional facilities are not very much different from those used in routine oilfield operations. Large quantities of chemicals will be injected over a long period, but it is not necessary to store large inventories of chemicals at the field site. Hence, the potential for environmental damage from storage and operation of the facilities is confined to a small area of the field and is limited to spills or leaks of less than the capacity of a railway car or truck. Precautions against health hazards to personnel using the chemicals in the field must be taken since all of the chemical compounds are severe irritants to mucous membranes.

Chemical compounds produced with the brine and oil are not a cause for concern because only a small fraction of the injected chemical is eventually produced. The amount of chemical injected in a chemical flood is designed to be approximately equal to the

or below the oil zone when it cannot be used in the brine injection program.

The major potential environmental problems associated with chemical flooding are: (1) Local air pollution by hydrogen sulfide removed from the produced brine during treatment, (2) Spills or leaks of chemical additives during transportation, storage and processing, (3) Health hazards from the dry chemicals and solutions, to personnel operating the field, (4) Leaks from surface storage and treatment ponds for produced brine, (5) Leaks from high-pressure pipes transporting mixed chemicals to the wells, (6) Underground leaks into shallow aquifers from damaged or corroded wells, (7) Production into shallow aquifers from improperly plugged abandoned wells (possible when the pressure in the oil reservoir is raised due to EOR activities,) (8) Production into aquifers above the oil reservoir through an incompetent seal above the reservoir (fracture or fault), (9) Subsidence along a fault plane caused by increase in reservoir pressure and (10) Subsidence caused by chemical disaggregation of the oil reservoir rock matrix.

### Micellar-Polymer Process

The micellar-polymer EOR process involves four separate phases of fluid injection beginning with a "preflush" injection of fresh or low salinity water, necessary to adjust the salinity and pH of the reservoir. The microemulsion is composed of a hydrocarbon, brine, surfactant, co-surfactants (generally alcohols) and electrolytes. The third injected fluid is a polymer solution whose increased viscosity assists in more efficient displacement of the oil bank and the microemulsion. Brine injection follows the polymer solution as the fourth fluid-injection phase.

Although the micellar-polymer process is considerably more complex, the environmental concerns are the same as those expressed for chemical flooding. The application of the micellar-polymer process increases the need for surface equipment and requires additional transportation, storage and a larger variety of chemical compounds. During the injection of chemicals (the second and third phases mentioned above) a large amount of chemicals will be injected in a relatively short time when compared to chemical flooding. Therefore, large inventories of



chemicals are required at the field site and several environmental concerns are intensified, but no new ones are added. Health hazards to personnel become greater because larger quantities of chemicals must be processed. Any leaks from surface storage or pollution of shallow aquifers from abandoned or incompetent wells going undetected for a long period would result in severe damage to ground or surface streams. However, recognition of intensified environmental concerns should result in more stringent design specifications of equipment and closer surveillance of operations. If abandoned or improperly plugged wells are suspected, monitoring of any fresh water aquifers along the hydraulic gradient during the chemical injection phases will be necessary.

In field tests of chemical flooding and micellar-polymer processes conducted so far, low-salinity water is used at various stages (preflush, surfactant solutions, polymer solutions, etc.). However, the trend is to design systems less sensitive to salt content and perhaps compatible with the produced oilfield brine. If this trend does continue and chemical solutions can be prepared in brines supplied by a brine aquifer and the oil reservoir, the presently foreseen socioeconomic impact of freshwater demand will be alleviated. If it is not possible to use oilfield brines for all of the chemical solutions by the time EOR processes are developed on commercial scales, a close analysis of water availability and negotiations for allocation will be required prior to implementation.

### Thermal Processes

Three types of thermal processes have currently gained widespread recognition: (1) the steam soak process, (2) steam drive, and (3) in situ combustion. Processes using steam are viable commercial enterprises for viscous oils in California where approximately 250,000 barrels of oil are produced each day by steam injection. DOE will soon conduct some pilot field studies in the mid-continent region to use steam for enhancement of oil recovery from deeper, less viscous oils than those of California.

Steam Soak: This process involves the injection of steam for 10 to 30 days, followed by a shut-in period to allow for heat transfer and penetration of the steam. The wells are then opened for the production phase of the process, which may last as long as 6 months. The actual duration of the periods of injection, soak and production depends on the characteristics of the oil, formation, and experience of the operator.

of in situ distillation, solvent extraction, and steam stimulation. Condensation of products of distillation, and gas expansion. Steam produces a zone of hot water that behaves as a hot water flood. The maximum anticipated oil recovery from the commercial projects now in progress is about 50 percent of the reservoir in place.

Environmental Aspects of Steam Stimulation: The steam processes require a constant source of fuel to generate steam along with an ample source of fresh water. Crude oil produced from the field, natural gas, processed fuel and coal are used for steam generation based on availability, economics, and air pollutant emissions. Water requirements depend upon the process used, total amount of steam required, and the ratio of the amount of injected steam (as equivalent amount of water) to the amount of oil produced, which may range from 0.1 to 5.0, or more. Water requirements gradually increase as depletion occurs.

The actual pollutant emissions from steam generation depend on a large number of variables such as the type of fuel and its chemical composition, the efficiency of heat exchange, design of the boilers and stack, and meteorology. If produced oil is used for fuel, approximately one-fourth of the production is consumed in producing steam. Emissions from a 50MM Btu/hr boiler may include:  $\text{SO}_2$  (10-25 kg/hr),  $\text{NO}_x$  (2-10 kg/hr), solid particulates (1-3 kg/hr), unburned hydrocarbons (0.2-0.5 kg/hr), and CO (0.5-1.0 kg/hr). These are very broad ranges, but it is not possible to present exact figures without measuring a specific installation over a long period. However, one can realize from the data that steam stimulation processes add a potential, and real, air-pollution hazard arising from direct-fired boilers. Since the total amounts of these pollutants must be maintained below State and Federal emission standards, the use of steam is constrained by the particular environmental standards involved. Perhaps this constraint could be lifted if the boiler flue gases can be cooled, compressed and added to the steam line, or injected separately into the oil-producing zone, to assist in production of the oil.

DOE has a contract with the Carmel Energy Co. to test a process in Kansas. The Vapor Therm process is designed to recover heavy oil by injecting a mixture of gases and steam to reduce the viscosity of the oil, dissolve carbon dioxide gas into the oil, and increase the reservoir pressure. The hot combustion gases (3,500° F) flow from the burners into a drum containing water where steam is generated by direct contact of the hot combustion gases with the water. The steam combined with the

combustion products is injected at the wellhead at 350°-650° F. In addition to its function as a steam generator, the water drum also acts as a scrubber for the combustion gases. The water removes corrosive components which are neutralized prior to injection of the steam. Many of the solid and corrosive components in the exhaust gas are trapped and neutralized in the steam drum. Although small amounts of the water in the steam drum must be removed regularly, atmospheric pollutants are almost entirely eliminated and beneficial results to oil production are obtained from injection of the combustion gases.

The demand for fresh water is a major consideration of steam-injection processes since water containing salts cannot be used because of severe, irreversible damage to the boilers. The steam is employed to improve the mobility of viscous crude oils that cannot be produced by other known techniques. Tests are also being designed to determine the feasibility of using steam-drive processes for enhanced recovery of less viscous oils in the mid-continent region. In all cases, the demand for water must be compatible with regional water availability to municipalities and agricultural interests; therefore, this is a major initial consideration for all proposed steam-injection projects. There are several other environmental concerns associated with steam-drive processes in addition to air emission from the boilers and the water demand. Large amounts of produced water must be separated from the oil, treated, and disposed of in accordance with existing state pollution-control regulations. Produced oil emulsions are frequently difficult to break and require special treatment for resolution. The entrainment of oil from oil-water separation and emulsion-breaking systems also requires close control because of the adverse effect it has on the water-disposal system. Provisions must also be made for disposal of solid wastes from scrubbers, boilers, tanks and flow lines.

In Situ Combustion: Several fire-flood pilot studies were made in the mid-continent region in the decades of 1950 and 1960 but at the time they proved uneconomical and did not attain commercial prominence. However, the pilot studies were very important in development of theories and technology unique to the process.

The in situ combustion processes are based on generation of heat within the reservoir by burning some of the oil in the reservoir. One procedure is simply the injection of air into a well followed by ignition of the oil and continued injection of air as the burning front expands radially around the well. Heat at the burning front (800°-1,200° F) produces steam, coke, distillation of the oil, thermal cracking of some of the heavy ends and pressure to move the front toward peripheral production

because the largest amount of heat dissipation, or transfer to the reservoir, occurs behind the burning front. The heat in the burned-out zone behind the front is of little value, but other methods have been devised to improve the heat transfer to the zone ahead of the burning front. One method that has gained recent prominence is the wet combustion process. After the burning front reaches a predetermined size, water is injected in place of air to act as a medium to transfer heat from the burned-out zone to the oil zone ahead. After an initial transfer of heat as steam, the burned-out zone is cooled. Continued injection of water results in a hot-water drive which reduces the viscosity of the oil and furnishes the driving energy to move the oil to the production wells. Other methods involving the transfer of heat to the oil zone by water are employed, (such as alternating injection of air and water) but detailed analyses of these are beyond the scope of this paper.

Air emissions from a well-designed in situ fire flood are minimal. The thermal cracking reactions at the hot combustion front produce light hydrocarbons that may escape during production at the surface along with some carbon monoxide, carbon dioxide and sulfur dioxide. However, the larger portion of these compounds probably remain confined in the reservoir.  $\text{NO}_x$  production generally is absent because the lower burning temperature does not favor their production.

Water produced with the crude oil can contain significant quantities of metals and metal oxides dissolved in the acid waters. These can cause contamination problems through spills and from leaks of the acid waters while they are being produced on the surface for subsurface disposal. The pH of the reservoir water may be lowered to 2.5, enough to cause severe corrosion of well casings in plugged (abandoned) wells and may lead to contamination of other aquifers communicating with the fire-flooded oil reservoir through the corroded segment of the abandoned

### Gas Flooding

Any process employing, or producing, a gas has a potential for air pollution which may be local (confined to less than 100 acres) or regional (covering several counties, or an entire state). Gas flooding is the introduction of gases, such as hydrocarbons and carbon dioxide, into the petroleum reservoir to improve oil-recovery efficiency through several theoretically beneficial effects: (1) The injected gas increases the reservoir pressure, furnishing energy to drive the oil to production wells. (2) By dissolving in the oil it reduces the viscosity and density of the oil and improves the mobility (ease with which the oil

may be injected directly into a gas cap above the oil zone to furnish a reserve of displacement pressure.

Before a decision to use gas flooding is made, a large, constantly available source of inexpensive gas must be near the oil field. Examples are a producing gas field or a gas-processing manufacturing plant producing one of the required gases as a by-product. The gas can be transported to the field by pipeline, truck or railroad tank car.

Transportation of the gases to the field by pipe, truck or rail is under strict regulation by both State and Federal statute. An accidental spill, or large leak, from any of these sources may cause severe local hazards including the possibility of a fire or explosion, but dissipation and dilution in the atmosphere will remove the hazard. One must also consider the fact that a viable economic incentive exists for not losing the valuable commodity being transported.

Water may be injected in large quantities in addition to the gas requiring the treating and processing of large volumes of water at the surface similar to operations of a secondary recovery process. The water is obtained from the produced water and recycled with added water obtained from a brine aquifer or nearby source of surface water. The water is generally treated for removal of solids, adjustment of pH, oxygen removal to reduce corrosiveness, and bacteria growth.

Air emissions at the field will generally originate from power facilities such as diesel or natural gas engines used in generating electrical power. Some hydrogen sulfide may also escape from the water-treating facilities. Other minor emissions may originate from storage tanks, vapor-recovery units and heat treaters.

The potential for surface or shallow ground water pollution is the same as discussed previously for any field project processing large quantities of brine at the surface for reinjection. Stored or impounded brine may leak, field pipelines may develop leaks, and well casings may crack or corrode during injection and production operations causing ground-water contamination. The potential of leaks and pipeline breaks have long been recognized as a result of secondary oil production. Because of strict State regulations, equipment design and constant monitoring, the likelihood of leaks and spills during enhanced oil-recovery operations is considered less than for conventional operations.

be placed in a pipeline if the hydrocarbon content is sufficient or it may be burned if the nitrogen and sulfur content will exceed ambient air-pollution standards, and the quantity produced is not sufficient to be of commercial value. Finally, it may be compressed and injected into the formation from which it was produced as a pressure-maintenance technique as well as for disposal.

## LEGAL ASPECTS

The Department of Energy has been mandated by law to assure the environmental aspects of all EOR processes, and to assure that the commercialized EOR technologies are environmentally acceptable. The EOR projects are required to meet Federal, State, and Local laws, regulations and standards. In this context, the laws are those regulations for the enforcement (by agencies such as the EPA) of standards established under the laws.

The National Environmental Policy Act of 1969 (NEPA), PL 91-190, requires Federal agencies to consider the environmental consequences of all actions that may affect the environment and to prepare Environmental Impact Statements for any major Federal actions that have a potential for an adverse effect on our environment. To implement the act, NEPA established the Council on Environmental Quality which presents guidelines to Federal agencies with respect to policy, responsibilities, planning and response elements, operations and coordinating instructions. DOE's NEPA implementation guidelines provide for an ongoing and continuous environmental appraisal and review process, including the preparation and publication of EIS.

The Clean Air Act and its amendments of 1970 and 1977 (PL 91-604 and PL 95-95) vested implementation authority in the Administrator of the EPA. Each state has the primary responsibility for assuring air quality within the state. EPA is instructed to compile a list of air pollutants to which the Act applies, prepare air-quality criteria, and determine ambient air standards for pollutants listed in the air-quality criteria.

EPA regulations implementing PL 91-604 include the National Air Quality Standards (NAAQS) Primary and Secondary Ambient Air Standards specified for sulfur oxides, particulate matter, carbon monoxide, photochemical oxidants, nonmethane hydrocarbons, and nitrogen oxide, and Performance Standards for petroleum refining and storage of hydrocarbon.

in areas such as California where the standards are exceeded in some cases. Compliance is site specific and can change if the standards are changed. Under the Clean Air Act Amendments recently passed by Congress, areas which have not attained NAAQS must do so by December 31, 1982. To achieve this goal, EPA is promulgating an emissions offset policy. Under this policy, no increase in emissions will be allowed unless there is a corresponding reduction in emissions from existing sources.

The Clean Air Act Amendments of 1977 allow states to prevent degradation of air quality by SO<sub>2</sub> and particulates where air quality is superior to the NAAQS. Under these provisions, states are allowed to classify their regions into three zones: Class I Regions (with very clean air) where only extremely small emission sources are permitted, Class II Regions where new sources with moderate emission sources are permitted, if the combined effects of all sources do not exceed the allowable increments of air-quality deterioration, and Class III Regions where emissions from new sources are allowed to the extent of compliance with the NAAQS. Since many of these regions have not yet been designated, it is difficult to determine whether EOR target regions will be subject to air-quality provisions that are too stringent, given the current environmental control technology for the processes.

New Source Performance Standards are also changing. For example, prior to passage of the Clean Air Act Amendment of 1977 EPA set a tentative deadline of February 1978 for proposing New Source Performance Standards for coal-fired boilers, which may apply to boilers fired by other fuels as well. The proposed standards cover particulate matter, sulfur dioxide, and nitrogen oxide emissions. Preliminary information indicates that standards will be proposed for small boilers which are the most common for EOR steam processes and are not currently regulated. Depending on how stringent the regulations are, new boiler installations may be required to add control technology not previously used at steam-injection sites. Similar regulations could also develop for other aspects of EOR processes as well.

The Federal Water Pollution Control Act provides the framework for regulation of waste-water discharge to surface waters. A National Pollutant Discharge Elimination System Permit is required under this act before waste-water discharge to surface waters from any source. The intent of the act and the discharge permits is to require use of the best technology economically available by 1983 and to attain and maintain receiving-water quality adequate to assure protection of public-water-supplied water used for agricultural and industrial operations, and the

oil-pollution prevention, and the National  
Elimination System covering discharge permits and certification

A major objective of the Federal Water Pollution Control Act was to prevent the discharge of pollutants into navigable waters, the contiguous zone and the oceans. The discharge of oil is prohibited, but under the provisions of the act pollutants do not include the injection of water, gas and other materials into wells to facilitate production of oil or gas. The regulation of oilfield operations is left to authorities within the oil-producing states. Therefore, the various states retain control of the injection of fluids in enhanced oil-recovery operations.

EOR activities may be regulated under the auspices of the Safe Drinking Water Act. Enhanced oil and gas-recovery processes are given special consideration under this act. The law states that Federal regulations for the state underground injection programs may not prescribe requirements which impede any underground injection for the secondary or tertiary recovery of oil and natural gas, unless such a requirement is essential to assure that underground sources of drinking water will not be endangered.

Although there are no Federal statutes, state water-use laws may present severe constraints to EOR development. Western states water riparian laws are aimed toward defining allocation for usage of the water resources. In essence, fresh water is a limited supply and competing demands for it must be addressed through this system.

The Occupational Safety and Health Act provides for the protection of workers by assuring a safe and healthful work environment. The Department of the Interior Regulations relating to pollution control and waste disposal include leasee requirements against pollution of streams and surface or underground waters. The Bureau of Land Management obligates leasees to take reasonable precautions to prevent soil erosion, damage to forage and timber growth, air and water pollution, damage to fossils, historic and prehistoric artifacts. The Bureau also requires the leasee to fill sumps and other excavations, remove or cover debris, and to restore the surface to its original condition at the end of field operations.



The environmental aspects of EOR require the acquisition of a considerable data base to: (1) assure compliance with state and federal laws, regulations and environmental standards, (2) to insure that a minimum of environmental disturbance occurs as a result of the EOR program, and (3) to alleviate any accidental environmental damage that might occur.

The constraints to EOR development from laws and regulation water availability, socioeconomic impacts, environmental monitoring programs, etc., are being assessed. In addition, some areas of research have been initiated to develop specific data. These will be described briefly.

Research has been initiated to determine the rates and products of decomposition of the chemical compounds used for EOR under laboratory-simulated subsurface conditions. This work will be used to analyze the long-term viability of the large quantities of EOR compounds injected during future commercialization of EOR technology. As a companion to this work, the dispersion and chromatographic properties of the EOR compounds are also being investigated under simulated reservoir hydrological conditions. These data will be employed to predict the long-term migration properties of the injected EOR compounds.

Biological degradation rates of EOR compounds by various cultures of bacteria is also under investigation. The data will be used to determine the natural decay rate of EOR compounds which may accidentally have polluted a segment of land or a shallow aquifer. Information on the degradation kinetics of specialized cultures may be useful to actively degrade spilled EOR compounds by inoculation with specially cultured bacteria.

The transport properties and natural chemical degradation rates of EOR compounds in shallow aquifers is also being studied to develop data that can be used to anticipate the migration pattern and decay of the compounds.

Studies are also being conducted to determine the circumstances under which the injected EOR compounds will initiate local seismic disturbances. In a related study, the reactions of the EOR chemicals with the cementing and supporting matrix of sedimentary geologic materials is under investigation. Data derived from this study will be used to determine whether long-term contact of the chemicals with sedimentary geologic material will disaggregate the strata and cause land subsidence to occur.

Other research specific to environmental concerns of EOR is anticipated as noted in the Environmental Development Plan (2).

In the study of the environmental aspects of enhanced recovery, eight areas are of concern: Atmospheric emissions, water use, groundwater impacts, waste-water effluents, solid wastes, occupational safety and health, physical disturbance and noise. These are being addressed for the overall EOR program in a Programmatic Environmental Impact Statement now being prepared. Each issue is also considered in individual Environmental Assessments of each field test site. Research has been initiated in areas where scientific data are not currently available to determine possible environmental consequences of commercial use of EOR technology.

Developments in Federal, State, and Local laws, regulations and standards are being followed closely to ensure compliance with DOE activities and to be informed as well as to assess the projected impact of the legal considerations on Enhanced Oil Recovery.

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## **SESSION 7**

### **CONTROL OF FOSSIL FUEL POWER GENERATION – CONVENTIONAL**

**Chairman: William Mott**

**Co-Chairman: Bernard Baratz**



Argonne National Laboratory

The development of new energy technologies carries with it a responsibility to identify and evaluate appropriate environmental control technologies and/or strategies. In the area of coal utilization, a continuing program for this purpose is being sponsored at Argonne National Laboratory (ANL) by the Division of Environmental Control Technology, Assistant Secretary for Environment, DOE.

As part of the program, in-depth engineering and economic assessments of available and near-term control technologies have been made by the ANL staff and several subcontractors. The topics covered include coal cleaning, NO<sub>x</sub> control, particulates collection, flue gas desulfurization and denitrification, low-Btu gasification with combined-cycle generation, and solvent refining of coal. The development of advanced technologies, such as MHD and fuel cells, is being monitored in-house together with such other fuel cycle elements as coal transportation.

Another important aspect of the program is the comparative evaluation of different control technologies. To facilitate this effort, an extensive data base of coal properties and reserve amounts has been established. All information to yield data from which estimates of cleanable reserves can be attempted. In order to use this large volume of data efficiently and speed the assessment task, computer models of control technologies are being developed for incorporation into a systems analysis framework representing the coal fuel cycle. To date, this framework has been used for several case studies of different power generation scenarios. These studies have included both eastern high sulfur coals and western low sulfur coals, and have utilized plant sites consistent with current practice. The comparisons have determined the least-cost mix of coal type and control technologies needed to meet current environmental regulations at each site, while at the same time producing electricity at minimum cost. Costs and energy usage for environmental control have been derived with respect to a reference 500-MW power plant. The effects of proposed regulatory changes have also been investigated and have been shown to produce significant increases in both power costs and energy usage for environmental controls.

At present, the ANL comparative assessment model is only applicable to conventional combustion techniques. As performance and economic data become available on advanced techniques such as fluidized bed combustion, MHD, liquefaction, and gasification/combined cycle systems, this information will be incorporated into the comparative assessment model. Once this incorporation has been completed it will be possible for the Department of Energy, other interested users, to evaluate the effects of these technologies on power generation while meeting environmental regulations on a site-specific

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and

H. Huang, Argonne National Laboratory

This paper is a synopsis of a study conducted for Argonne National Lab to examine the effectiveness of combustion modification methods for NO<sub>x</sub> applicable to coal-fired industrial boilers including low excess air, combustion and burner modifications. Boiler types considered included and underfed stokers, spreader stokers, pulverized and cyclone fired u

Baseline (as-found) NO<sub>x</sub> emissions from grate fired stokers were shown the range of 200 to 300 ppm. Similarly, as-found emissions from suspe fired units were quite low as compared to comparably designed utility Low excess air was shown to be the most effective method on existing u emissions by approximately 10%. Evaluation of staged combustion and b fication, however, were limited due to current boiler designs. Major modification/design and implementation are necessary before the potent techniques can be fully evaluated.

The study emphasized the numerous operational factors that are of majo to the user in selecting and implementng a combustion modification inc energy considerations, incremental capital and operating costs, corros secondary pollutants and retrofit potentials.

#### THE LOW NO<sub>x</sub> HEAVY FUEL COMBUSTOR CONCEPT PROGRAM

John R. Facey  
U.S. Department of Energy  
Energy Technology

and

Richard W. Niedzwiecki  
NASA, Lewis Research Center

The objectives of this program are to generate and demonstrate the technology required to develop durable gas turbine combustors for util and industrial applications, which are capable of sustained, environm acceptable operation with minimally processed petroleum residual fuels. The program will focus on "dry" reductions of oxides of nitrogen (NO<sub>x</sub>) and improved combustor durability while maintaining high efficiency.

or shale); acceptable exhaust emissions of carbon monoxide, unburned hydrocarbons, sulfur oxides and smoke; and retrofit capability to existing engines.

## ASSESSMENT OF ENERGY AND ECONOMIC IMPACTS OF PARTICULATE CONTROL TECHNOLOGY IN COAL-FIRED POWER PLANTS

V. Ramanathan  
S. Reigel  
P. Gorman  
P. Reider

Midwest Research Institute

Midwest Research Institute has carried out a project, under a contract with Argonne National Laboratory, to assess the economic and energy impacts of particulate control systems in coal-fired power plants. The assessment was based on major functional variables such as plant size (100 to 1,000 MWe), location, coal type, and emission standards. The work on this program resulted in the generation of algorithms, to predict equipment cost, installation costs and energy usage for various particulate control devices. The devices considered were electrostatic precipitators (hot side and cold side) fabric-filters (reverse air and shaker types) and wet scrubbers.

First, a boiler performance model was developed using variables such as plant size, coal characteristics, etc. The output from this model (i.e., flue gas flow rate, grain loading, etc.), then was utilized in control device performance models to generate required design and operating parameters for the control systems under study. These design and operating parameters were then used in the cost models.

The cost models aggregate three cost items: the first costs (capital investment), total first-year annualized costs and the integrated cost of ownership and operation of the control equipment over an assumed plant lifetime of 30 years. The models have been programmed for speedy computation. However, the algorithms are easily solvable with a hand calculator. In addition, suitable guideline values have been provided for independent variables wherever necessary. Ample case studies are presented to demonstrate use of the models.

U.S. Department of Energy  
Grand Forks Energy Technology Center

Fly ashes from the combustion of many Western and Gulf Coal lignites and bituminous coals contain high concentrations of alkali which can be used in a wet scrubber for removal of  $\text{SO}_2$ . Additionally, dry methods of flue gas desulfurization will be required for new and retrofit power installations in water-scarce areas in the Western U.S. The Grand Forks Energy Technology Center of DOE has performed tests on utilizing fly ash in lieu of lime/limestone in a 130-scfm laboratory scrubber and a 5000-acfm pilot scrubber operated on a flue gas slipstream at a utility burning North Dakota lignite, and on dry sorbent injection techniques in a 75-lb/hr pulverized coal-fired pilot combustor.

In this report, experimental results are presented on: 1) utilization of fly ash alkali in a wet scrubber; and 2) a series of tests designed to evaluate trona and nahcolite as dry sorbents for  $\text{SO}_2$  control. Ash alkali wet scrubbing results include the correlation of  $\text{SO}_2$  removal, alkali utilization, and scale formation with operating conditions such as feed stoichiometric ratio (Ca/S), liquid-to-gas ratio (L/G), pH, and the concentrations of suspended dissolved solids. Results on dry absorption of  $\text{SO}_2$  include injection of dry sorbent into flue gas with subsequent collection in 1) a pilot ESP, and 2) a pilot baghouse. Temperatures of injection and residence times were varied to simulate full-scale conditions; the points of injection ranged from direct addition into the flue gas along with the coal, to addition at the inlet of a cold-side ESP or baghouse. Data on  $\text{SO}_2$  removal efficiency and reagent utilization are correlated with operating conditions. A parallel laboratory study on the kinetics of reactions between the dry sorbents and flue gas  $\text{SO}_2$  and  $\text{NO}_x$  are also described.



Meyer Steinberg, Anthony S. Albanese, and Vi-Duong Dang

Brookhaven National Laboratory

C. F. Baes, et al, Oak Ridge National Laboratory

Gregg Marland, Institute for Energy Analysis

The possible adverse global environmental effects of CO<sub>2</sub> buildup due to fossil fuel energy utilization have prompted an investigation of possible methods for its control. A systematic overview is presented for various routes for removal, recovery, disposal and use of CO<sub>2</sub> from various control points in the global system. The effect of substitute alternative non-fossil energy sources on the global CO<sub>2</sub> problem is evaluated. The energy and mass balances for a number of removal and recovery routes are used as evaluation criteria. Flow sheets are presented for conversion of CO<sub>2</sub> from various sources to synthetic carbonaceous fuels with the use of non-fossil energy. Several unique CO<sub>2</sub> disposal alternatives are presented and discussed.

#### THE IMPACT OF COGENERATION UPON EMISSIONS

Eric Lister

U. S. Department of Energy  
Energy Technology

The objective of this paper is to highlight why an energy conservation technique such as cogeneration is of primary interest to a Fossil Energy group whose major criteria for success is the utilization of coal. The paper will show the following:

- 1) That cogeneration can reduce the emissions/useful output by a factor of 3 to 5 and is therefore one of the leading technologies for the acceptable utilization of coal and coal-derived fuels.
- 2) That if cogeneration on coal and coal-derived fuels is to become prominent in the industrial and commercial/residential sectors it will require the continual development of (a) heat engines to handle the harmful agents in these fuels (b) heat recovery equipment so they can be cogenerated and (c) an on-going effort to identify and develop other critical technologies needed to make coal cogeneration the success that it promises



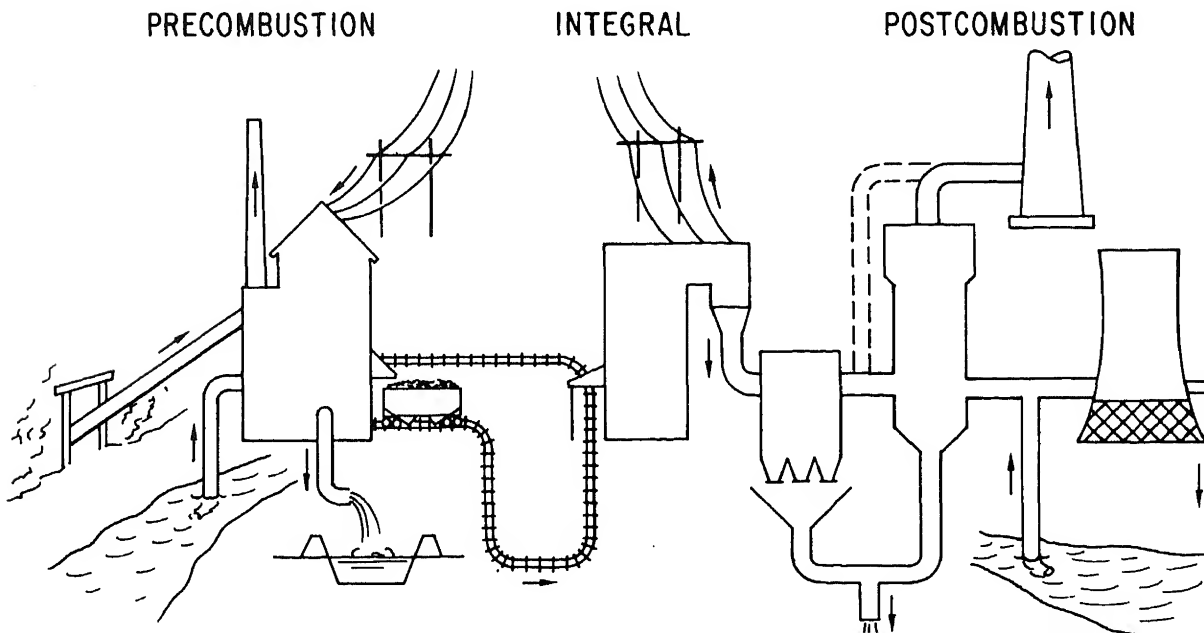
K.E. Wilzbach, C.D. Livengood, and P.S. Farber  
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## 1 INTRODUCTION

The Environmental Control-Coal Utilization Program is a continuing Argonne National Laboratory (ANL) effort sponsored since 1976 by the Division of Environmental Control Technology, ASEV/DOE. It provides in-depth evaluations of the technical, environmental, and economic aspects of control technologies for coal-based energy systems, as well as systems comparisons of alternative control technologies and/or strategies. The program was developed in response to a need within ERDA, predecessor to DOE, for independent evaluations of the capabilities of existing technology and reviews of ongoing research and development programs. In this way, the program assists the Environment staff in fulfilling its responsibility to assure the adequacy of environmental control systems for fuel extraction, conversion, and utilization.

Subjects under evaluation span the coal fuel cycle from mine mouth to waste disposal, as shown in Fig. 1, and include both current and developing

## ENVIRONMENTAL CONTROLS



realize that while these subdivisions are common, the techniques are truly independent of other parts of the system. The techniques are in fact so pervasive and far-reaching that a systems analysis is demanded for a complete assessment of any of the components.

This systems perspective, coupled with the use of in-depth analyses, places the ANL program in a unique niche within the assessment efforts, being both more comprehensive than studies of a single control technique or pollutant and more detailed than regional or national energy assessments. Our approach begins with information on the costs, reliability, energy requirements, and secondary effects of pollution control systems from reports and discussions with manufacturers, users, and developers of the process. In this effort, the capabilities of the in-house staff are supplemented by the able use of subcontractors and consultants with special capabilities and expertise. Evaluation of this information leads to the identification of problem areas, inherent process limitations, and high-payoff areas for research and development.

Further, the information on individual processes is part of a program of technology comparisons that use a computerized systems-analysis methodology. These comparisons are used to identify the potential for new technologies as a function of environmental regulations, location, and time of development. In cases where several approaches appear to be viable, it is often possible to identify critical process parameters and the most effective in altering the existing balance or that are required for small changes in environmental requirements.

The initial studies performed in the program were devoted to surveying available technologies/strategies for the control of pollutants ( $\text{SO}_2$ ,  $\text{NO}_x$ , and particulates) from coal-fired utilities. These were presented in our first report, ANL/ECT-1, together with a summary of existing federal and state environmental regulations and the effects of pollutants. Some attention was also given to the control of air pollution, disposal of solid wastes, and the status of fluidized bed combustion (FBC) technology. Information gathered in that first series of studies has subsequently been used to identify and scope more detailed assessments performed by subcontractors to ANL, resulting in a series of reports dealing with individual control technologies. In addition to these studies, the ANL staff has been analyzing areas of technology not previously covered and has begun to study advanced technologies under development. All of these assessments are briefly reviewed in the following section. The third part of the paper presents the results of a typical technology comparison based on alternative regulatory

The technology assessments performed to date have focused on available and near-term technologies in order to establish an information base suitable for technology comparisons and for the evaluation of environmental regulations that may affect coal-based energy systems. Data will also serve as benchmarks in analyses of mid-term technologies. Several such studies are now being developed by the program staff and will be noted in the following discussion.

## 2.1 PRECOMBUSTION CONTROLS

Precombustion, as defined in this program, encompasses all operations from the mine mouth up to the fuel utilization step (the boiler, industrial systems). It can range from a simple conveyor belt and storage in the case of a mine-mouth plant to complex arrangements involving multiple stages of transportation and storage coupled with coal conversion to an alternative form.

### 2.1.1 Coal Transportation

Transportation facilities (rail, barge, truck, pipeline) are significant in determining both the availability and delivered cost of specific coals or coal products. Thus, the fuel choice at a particular plant, and, through the fuel characteristics, the selection of environmental controls can be influenced by the transportation system. There may be a significant consumption of fuel or other resources and production of pollutants during transport, although the latter are admittedly widely distributed. However, these transport-related pollutants will become more noticeable in the system evaluation as on-site emissions are lowered.

An extensive survey of the available literature on coal transportation has been made by the program staff with particular emphasis on environmental effects and costs. This information will be incorporated into future comparative systems evaluations.

### 2.1.2 Coal Preparation and Cleaning

By far the most extensive effort in the precombustion area is an assessment, performed by Bechtel Corporation, of coal preparation and cleaning technology. That study addressed current industry practices, developing methods for both physical and chemical cleaning, as well as the effects of cleaning on important coal properties. Detailed flow sheets were used to generate estimates of costs and environmental impacts due to cleaning of specific coals. Although the results were far too comprehensive to summarize here, one can conclude that significant sulfur reductions are possible for carefully selected coals if fine-coal cleaning is employed. However, the technique carries with it potential environmental problems in the development of a large-scale cleaning facility.

from the U.S. Bureau of Mines, about 10% of the reserves were matched with washability data and merged into a single data file. This included 35% of the reserves that account for 80% of production.

### 2.1.3 Solvent Refined Coal (SRC)

More extensive coal processing is represented by the SRC-1 (solid product) and SRC-2 (liquid product) technologies. A preliminary study of the literature and pilot plant results for SRC-1 was performed for Owens-Illinois Air Products and Chemicals, Inc. That project also included determining product costs and material and energy balances for a 20,000-ton-per-year feed plant. Product costs were estimated at about \$3.25/10<sup>6</sup> Btu for a delivered coal costing \$25 per dry ton. Finally, the properties of SRC-1 as a fuel were discussed relative to conventional pulverized coal. A need for some burner redesign was identified, as was a potential for high NO<sub>x</sub> emissions.

A more recent study conducted by the ANL staff surveyed the monitoring results obtained at the Ft. Lewis pilot plant. No meeting existing air and water standards were identified, but the limitations of the plant and the limited testing data available preclude any conclusions at this time.

### 2.1.4 Coal-Oil Mixtures (COM)

The use of COM has been widely discussed as a potential fuel for existing boilers. It would further the nation's goal of greater coal utilization while, it is hoped, creating minimal environmental problems. A preliminary study of this technique by the program staff has revealed high degrees of success in producing, storing, transporting, and firing COM. The ways in which different oil and coal properties affect the COM and the consequences of prolonged use are not well-defined.

Some add-on flue-gas cleanup controls will probably be required for COM use, but the requirements will vary with the sulfur contents of the coal and oil used, as well as their relative proportions. This is due to the fact that the applicable regulations are generally a combination (on a weight percent basis) of those for coal and oil taken separately.

## 2.2 INTEGRAL CONTROLS

Taking advantage of inherent system characteristics to achieve environmental control goals is obviously attractive insofar as it reduces

excluded as an adequate stand-alone technique by the percentage requirements of new environmental standards. The other integration options studied by the ANL program and described in this section are viable, but their vulnerability to regulatory change should not be overlooked.

### 2.2.1 Combustion Modifications for NO<sub>x</sub> Control

An analysis of combustion modification techniques for NO<sub>x</sub> utility boilers was performed by KVB, Inc. It identified staged and low-excess-air operation as the most cost-effective methods for existing units. For new units or extensive retrofits, improved burner design was found to offer promise of even greater reductions. There is considerable variation in the NO<sub>x</sub>-reduction potential between various combustion boiler type and combustion modification, but the reductions now achieved on commercial units are generally less than 50% and typically only 20-30%. Additional concerns are centered mainly on unresolved questions about emissions arising under these operating conditions.

KVB is presently developing an update of this report to include developments in the field during the past year. Also, they have completed a similar study of NO<sub>x</sub> control through combustion modification on industrial boilers. Similar techniques are used, but the analysis is complicated by the wide variation in furnace types and sizes. This work was initiated in anticipation of increased policy interest and regulatory action related to the industrial use of coal.

### 2.2.2 Fluidized-Bed Combustion (FBC)

The possibilities inherent in FBC for integral control of sulfur emissions while providing economic power for utilities and industry have been discussed. The strong base of information that exists at ANL for FBC technology has enabled the program staff to develop assessments of FBC advantages and existing or potential problems. One such study is now in progress.

However, in order to obtain an independent point of view, MPR Corporation has been engaged to analyze results reported at the 5th International Conference on FBC held in December 1977. They have had access to these data as conference organizers. The method used may be unique in the way data, issues, problems, and information gaps are presented in matrix form. Also, it uses a linear approach to conclusions and development that is independent of prior knowledge regarding issues or options. This may be regarded as either a strength or weakness, depending on the needs. This work is now nearing completion.

(IGT), and entrained-flow (Foster Wheeler) gasifiers processing and Montana coals. With this work as a basis, a more extensive has been undertaken by United Technologies Research Center. In the above gasifiers, a Texaco unit is being included in this study both Illinois bituminous and low-sulfur Montana subbituminous coals used in the analyses. This work is now nearing completion.

Both studies have found the G/CC systems to emit lower quality pollutants than conventional power plants and to be economically competitive with existing technologies. However, the wide band of uncertainty associated with these cost estimates precludes any firm conclusion at this time. This uncertainty is largely due to the need for further development of both gasifiers and the advanced high-temperature gas turbines required. These developments will be crucial to commercialization of this technology, since significant cost advantages must be shown before a novel approach will be accepted by the utility industry.

#### 2.2.4 Other Developing Technologies

Assessments of two additional coal utilization technologies incorporating integral controls are now being planned. Advanced molten fuel cells may offer unique siting opportunities as well as highly efficient coal utilization. The cells are generally viewed as environmentally friendly but the environmental control aspects of the fuel conversion process and its relationship to the fuel cells merits analysis.

Power plants based on magnetohydrodynamics (MHD) also promise of high efficiency. An upcoming study will explore numerous unanswered questions regarding the efficiency of both integral and modular systems and the environmental controls for this technology.

### 2.3 POSTCOMBUSTION CONTROLS

Most questions about environmental controls have been centered on the costs and effectiveness of postcombustion cleanup systems. For this reason, a very significant part of our program's effort has been devoted to this area.

#### 2.3.1 Particulate Collection

Several studies have been devoted to the assessment and development of particulate collection systems. The first of these, conducted by the Research Institute, discussed the sources and characteristics of particulate emissions, applicable emission regulations, available technologies, technical



on a combination of emission regulation, coal sulfur and ash content characteristics.

In order to further explore the tradeoffs between different Midwest Research Institute was engaged to develop energy and economic of available particulate collection equipment suitable for our evaluations. That model supplements a previously developed computer written at ANL (see Sec. 3.1).

Another study was performed at Manhattan College with the assessing collection techniques for fine (submicron) particulate. Particles in this range are of great concern, because they are respirable may carry toxic trace elements. Topics addressed in the study include formation and characterization of fly ash for different coal and boiler the performance of both conventional and novel devices, and energy, and operational aspects of the alternatives. Baghouses were identified as the most attractive option among available alternatives as emissions are tightened, although ESPs may be competitive for high-temperature pressure applications. Novel devices under development were judged to have little promise for improvement in fine-particulates control before the best.

At the present time, we are sponsoring a study by KVB, Inc. to investigate any correlations between combustion conditions and particulate emission. If sufficient data are found to be available, this study will lead to a better understanding of how particulate control is influenced by and combustor characteristics.

### 2.3.2 Flue Gas Desulfurization (FGD)

No other area under the purview of this program has been the subject of such controversy as FGD. This is due to a number of factors, including strong regulatory pressure for development, a limited base of experimental utility applications, and the lack of firmly established "standard" or design procedures that consistently produce satisfactory performance.

A study surveying the status of FGD, worldwide as well as in the U.S., was performed for us by the Tennessee Valley Authority (TVA). More than 20 different process types were identified. These were divided equally between those yielding throwaway and recoverable products. The only significant experience in this country is for throwaway limestone (L/LS) systems, which comprise about 95% of the operating systems on a megawatts-served basis. The study identified numerous operational problems and high maintenance requirements for these systems. It pointed out that there is as yet very little experience with FGD fired with high-sulfur coal.

Subsequent projects by both TVA and Batelle Columbus Laboratories have sought to utilize the available data to model performance and

If regulatory requirements for  $\text{NO}_x$  reduction in stationary sources are increased, the combustion modification techniques noted in Section 2.3.3 may no longer be adequate. In anticipation of such a possibility, Westinghouse Electric Corporation (WEC) is planning to include in the  $\text{NO}_x$ -control study mentioned previously a study on gas-phase reduction of  $\text{NO}_x$ . Ammonia injection appears promising, but large-scale coal-fired tests are needed to verify its effectiveness and to investigate costs and secondary pollutants.

In another assessment, TVA reviewed processes currently being developed for the simultaneous removal of  $\text{NO}_x$  and  $\text{SO}_2$  from flue gases. Of the such processes, most Japanese in origin, were evaluated in some detail. The most advanced types were found to be dry selective catalytic reduction, wet oxidation-absorption-reduction. However, further process development, scale-up, and application to flue gas from coal-fired boilers are needed before realistic assessments of their potential roles in the U.S. can be made.

#### 2.3.4 Solid-Waste Disposal/Utilization

The question of solid-waste disposal has been reviewed by ANL staff and several subcontractors in connection with studies on air pollution control, FGD, and FBC. In general, the concerns identified involved about cost, questions of land-use policy, and the possibility of water pollution through leaching. Passage of the Resource Conservation and Recovery Act (RCRA) has greatly increased concern regarding this question because vastly increased disposal costs could be in the off view of this area is planned pending an evaluation of the regulations formulated by the EPA.

#### 2.3.5 Waste-Heat Disposal/Utilization

The disposal/utilization of power plant waste heat is rightly considered as an environmental control technology, and one that has been the subject of considerable controversy. Assessments of the technical, performance, and economic factors associated with the various techniques are now being planned to supplement preliminary data gathered by the ANL staff.

The comparative assessments draw upon information generated from detailed technology evaluations. These comparisons can involve the coal-to-power system, or they may focus on specific system elements such as particulate control. In order to provide this flexibility, a modular approach is used wherein each module represents a significant, functionally separable, component of the system. The modules are gradually computerized as sufficient data become available through the acquisition and development of models. Several computerized data bases are also included to serve as sources of input information for the comparisons.

### 3.1 MODELS AND DATA BASES

One data base was the result of the effort described previously to integrate coal reserve and washability data. At this time, integration has been achieved for 189 different state/county/bed combinations. However, the fact that many coals were tested more than once leads to a total of more than 100 integrated data sets. Present plans call for significantly expanding the sample using additional washability information collected recently.

A related data base has been developed using the Bureau of Mines coal reserve and analytical data tapes. More than 56,000 separate entries are available in the base. The information is useful in providing input for coal analyses for the evaluation of control performance, identifying differences in coal characteristics, and assessing coal variability.

Modeling efforts by subcontractors to the program have been described in the preceding sections. These efforts have included the entire power generation system, FGD, and particulate control. The ANL staff has been active in this area with the development of a particulate control model incorporating cost and performance information for ESPs, baghouses, and scrubbers. The model calculates energy consumption, capital cost, and incremental electricity cost for each option as a function of coal properties, plant size, and regulatory constraint. An example of the program output is shown in Fig. 2 for a comparison involving a slightly cleaned, low-sulfur eastern coal. Note that the most economic options in this case are the ESP and the baghouse, with the hot ESP favored under present NSPS (0.03 lb/10<sup>6</sup> Btu) and the baghouse having a slight advantage under the proposed NSPS (0.03 lb/10<sup>6</sup> Btu). This type of analysis was used to select the least-cost option for each regulatory alternative in the following comparison.

### 3.2 EXAMPLE COMPARISON

Recent months have seen a vigorous debate waged over the proposed revisions to the federal New Source Performance Standards. For this study, we have developed a comparison of two plausible regulatory scenarios applied to the reference case described in Table 1. The environmental requirements specified in Table 2 were added as needed, and adjustments were made to the

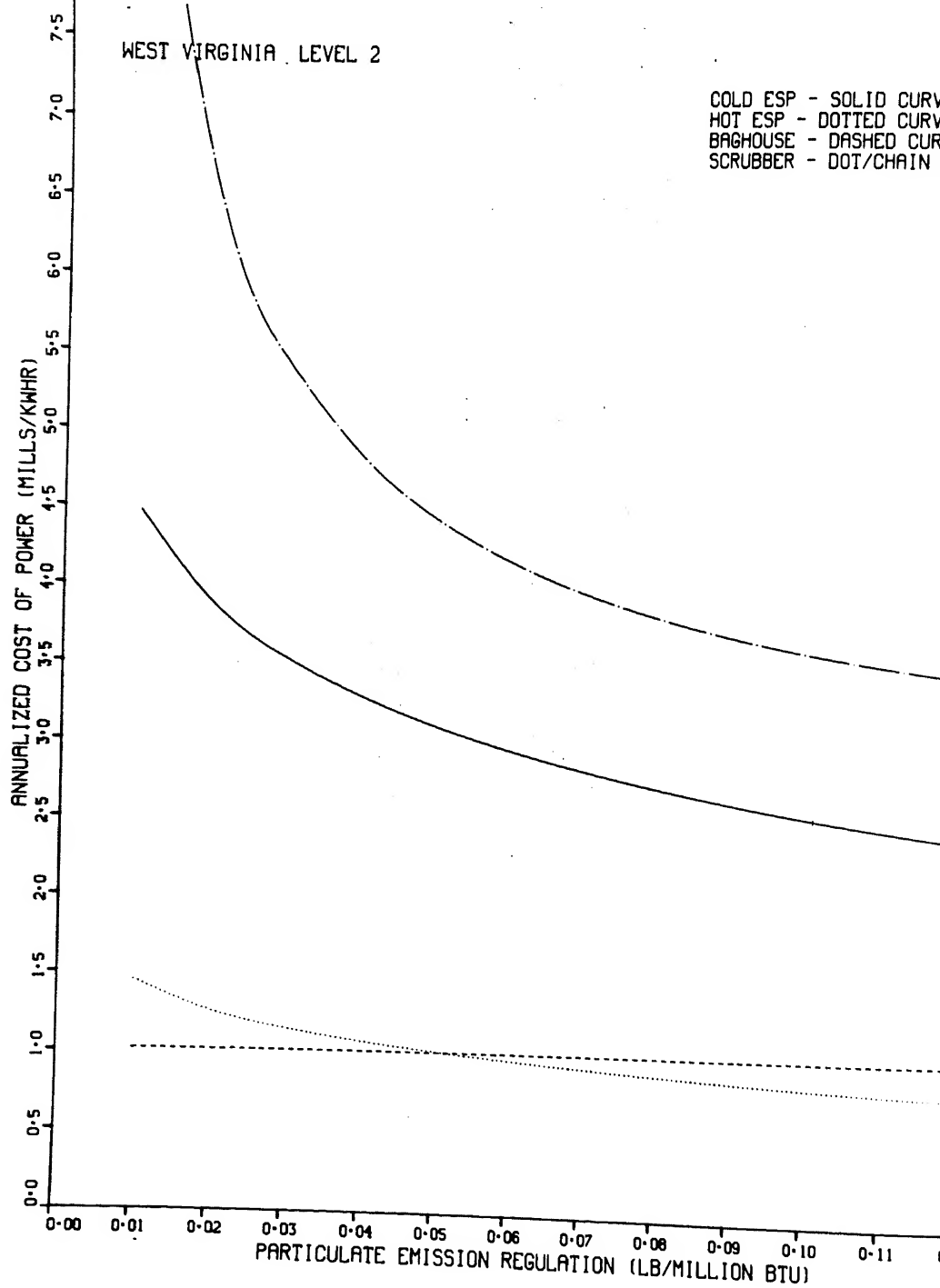


Fig. 2. Cost/Performance Tradeoffs from ANL Particulate Collection Model

Location	Northern Illinois
Net output	500 MWe
Type	Conventional pulverized-coal fired
Heat rate	9200 Btu/kWh
Environmental controls	None
Coal characteristics (as received)	10,500 Btu/lb, 16% ash, 0.6, 1.0, 3.0, or 5.0% sulfur

Table 2. Environmental Controls

Particulates	Lowest cost option chosen from hot or cold and baghouses.
SO <sub>2</sub>	Limestone slurry FGD with combined fly ash sludge disposal in a clay-lined pond.
NO <sub>x</sub>	Combustion modifications.
Cooling	Wet mechanical draft cooling towers instead the reference-case once-through cooling.
Water Treatment	System corresponding to the best available technology.

The object of this comparison is to illustrate the costs corresponding to different levels of environmental control. These costs are compared with certain benefits to society, foremost of which are the 500 MWe of electricity produced by the plant. However, while a cost-benefit analysis is conceptually appealing for arriving at the optimum control level, it is prevented at this time by uncertainties in pollutant-damage estimates and the lack of a consensus on the costs of health effects. Therefore, we present the costs separately in terms of economic penalties applied to the production of power, residual pollutant emissions, and the consumption of

Air pollution regulations used for this example are shown in Table 1. Two different sulfur control levels were used, since this is the area of greatest sensitivity for costs and performance. These alternative levels range from the pond to the full scrubbing requirement recommended by the EPA, with the removal determined on the basis of either daily or monthly average concentrations. Four different coal sulfur levels were used, as shown in Table 1.

NO <sub>x</sub>	0.1 lb/10 <sup>6</sup> Btu
Particulates	0.1 lb/10 <sup>6</sup> Btu
SO <sub>2</sub>	1.2 lb/10 <sup>6</sup> Btu
Alternative NSPS:	
NO <sub>x</sub>	0.6 lb/10 <sup>6</sup> Btu
Particulates	0.03 lb/10 <sup>6</sup> Btu
SO <sub>2</sub>	85% removal or 92% removal, both with a maximum level of 1.2 lb/10 <sup>6</sup> Btu and a minimum require level of 0.2 lb/10 <sup>6</sup> Btu

---

pliance with the present NSPS with no additional controls, while a fur some flue-gas bypass could still be used to eliminate reheats. Both of these low sulfur coals require full scrubbing under alternative standards. The 3% sulfur level is representative of many utilities and requires FGD in all cases. At 5% sulfur, the "ceiling" comes into play since greater than 85% removal is required a level of 1.2 lb/10<sup>6</sup> Btu. Thus, these four sets of coal properties yield a representative spectrum of SO<sub>2</sub> control costs under all of the considered.

Based on the foregoing assumptions, the incremental electricity costs (in 1980 \$) and pollutant burdens associated with the environmental requirements are presented in Figs. 3 and 4. Note that they are expressed as dollars or lb/MWh in order to more directly relate costs and benefits. The format illustrates how, when regulations are based on energy intensity (lb/10<sup>6</sup> Btu), the addition of energy-intensive environmental controls for one pollutant can actually increase emissions for others. For inspection of Fig. 3 shows that the addition of scrubbing for SO<sub>2</sub> of increasing coal sulfur (under present NSPS) serves to increase emissions of NO<sub>x</sub> and particulates emitted, since the plant heat rate changes from 9500 to nearly 10,000 Btu/kWh. This effect on performance is shown dramatically in Fig. 5, where the energy consumption due to control requirements. For low sulfur coals, the energy requirements for pollution control are more than doubled under the proposed changes.

The incremental economic costs shown in Fig. 3 are due primarily to increasing FGD requirements that result in both additional equipment and large increases in the amount of solid waste requiring disposal (in Fig. 4). It is clear from the figures that there is a trade-off between electricity cost and pollutant emissions and that the change in SO<sub>2</sub> regulation also changes the form of the cost balance. Under the present NSPS, emissions are fairly uniform across all coal types, and

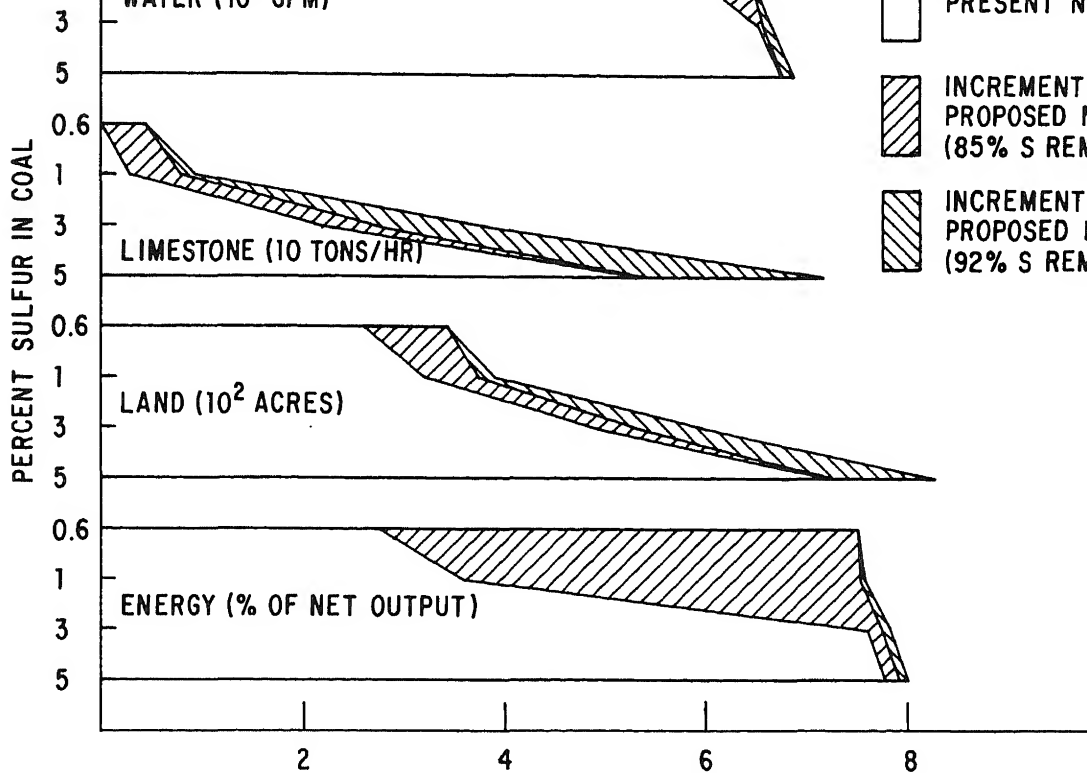


Fig. 5. Resource Consumption by Environmental Controls

delivered prices, the economics favor the use of low sulfur coal. other hand, a fixed percentage-reduction requirement for SO<sub>2</sub>, couple very low "floor," greatly reduces the cost differential while produc variations in emissions. This acts to favor the use of local coals areas of the country. However, where that implies a shift from low-sulfur coal use, air emissions will not be significantly reduced a wastes will increase by a factor of 2-4.

Resource requirements, as shown in Fig. 5, also increase requirements are dominated by condenser cooling, so that the increa the addition of FGD is less dramatic than one might anticipate. this is a very site-specific item, and the choice of a less humid would result in increased water losses because of waste-pond eva The sludge pond is also responsible for the increases in land requ These closely follow the changes in solid-waste burden, since a cons depth of about 20 ft was used in the calculations. Note that the c land-use impacts due to FGD are somewhat damped by the existing ash disposal.

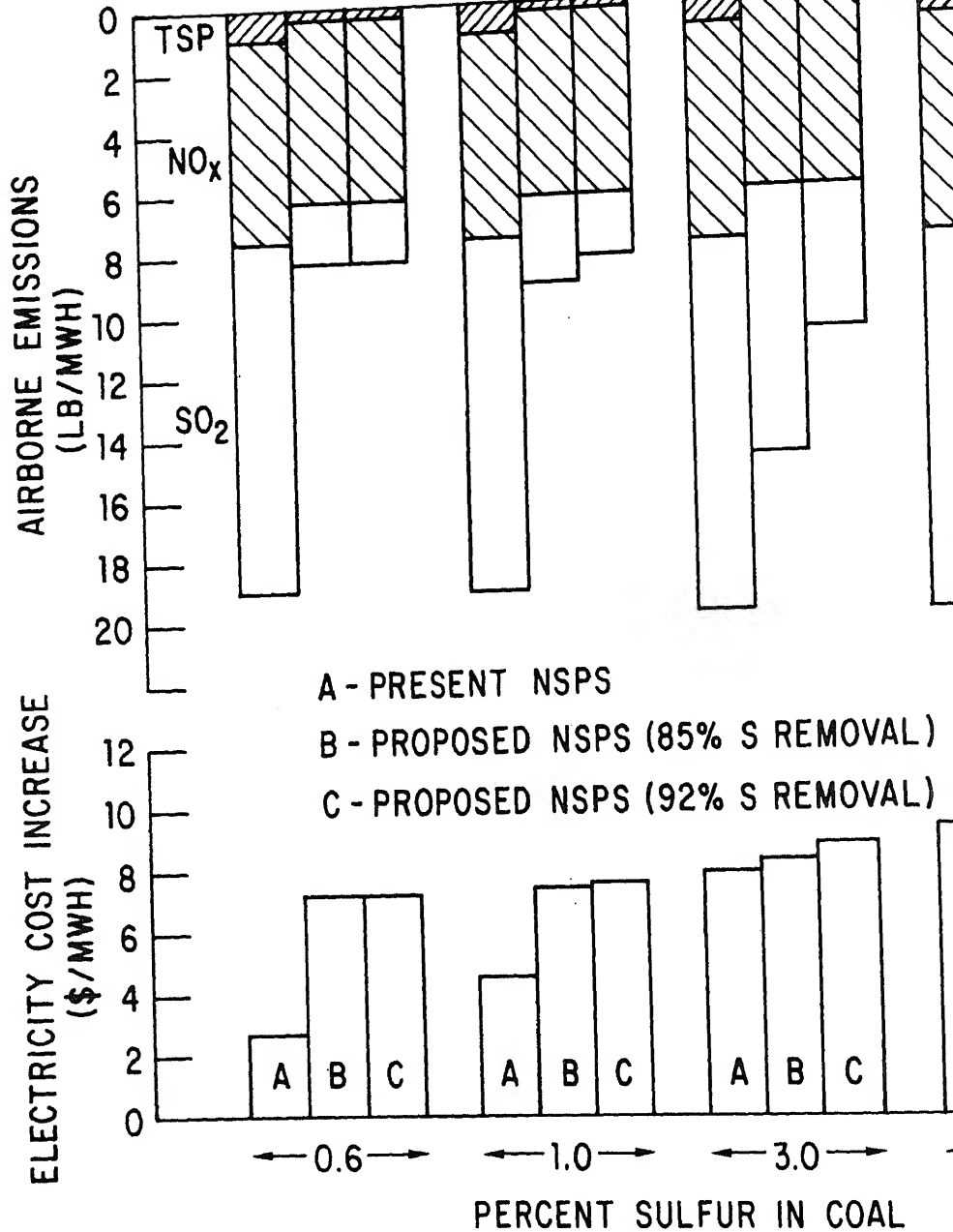
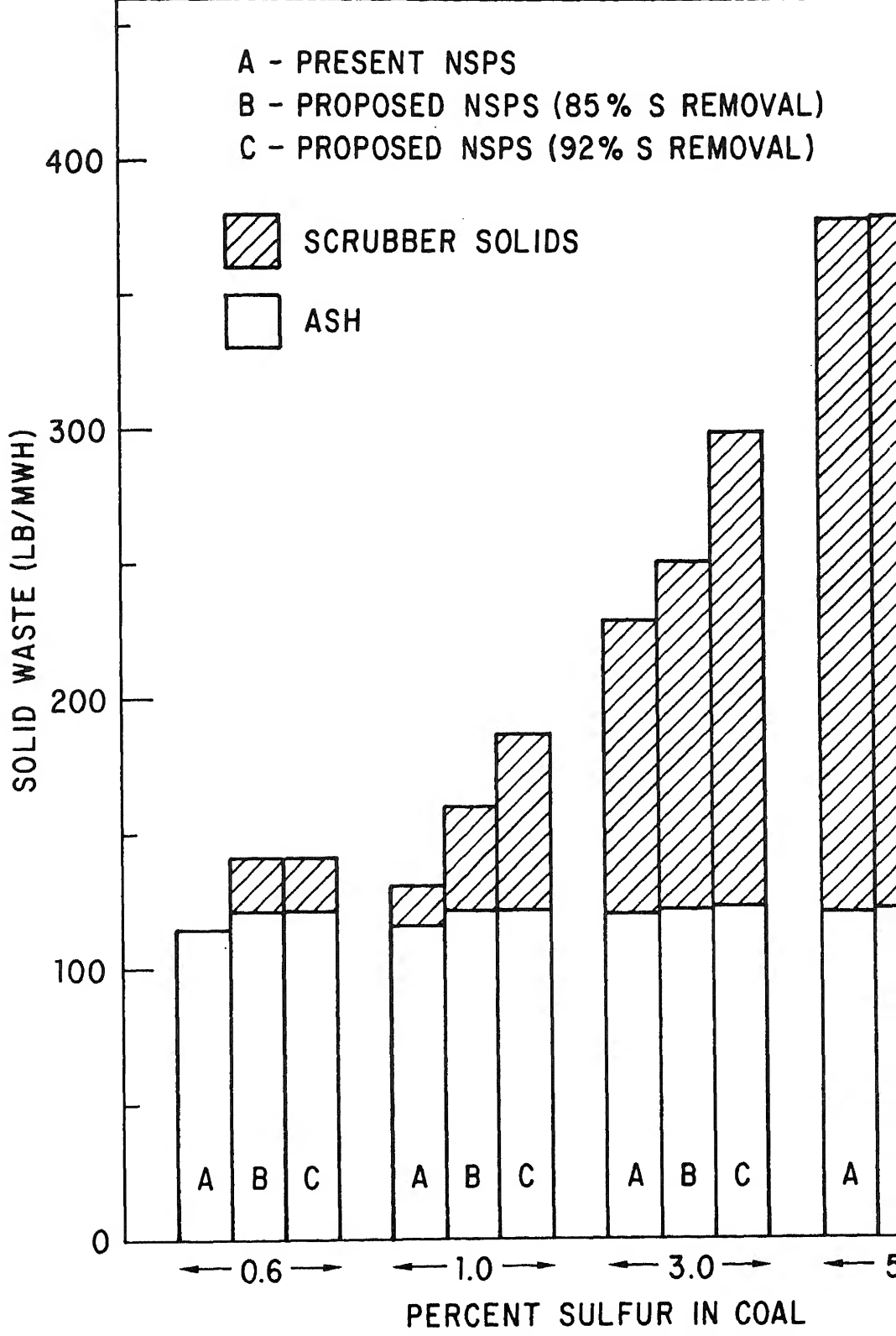


Fig. 3. Environmental Control Costs and Residual Air Emissions





## 4 CONCLUSIONS

The preceding example has provided ample indications of how environmental controls affect other parts of the energy system and the environment (air, land, and water). If precombustion controls had been analyzed, more far-reaching interactions would have been seen. Thus, it is clear that a systems perspective be adopted and faithfully followed in evaluating the performance of controls, the desirability of regulatory changes, and the environmental aspects of research and development programs.

The many tradeoffs between costs and benefits also argue for basing emission restrictions on energy output rather than on emissions. This would not only provide a more direct measure of the cost/benefit tradeoff but would also promote the use of efficient controls and conserve resources by providing an additional incentive for efficient plant operation. For example, it could greatly enhance the attractiveness of measures to utilize waste energy, as in cogeneration. Figure 6 illustrates for particulate emissions that emissions are presently a function of heat rate (plant efficiency). The line shown by the upper and lower lines. The middle line shows how a system based on output energy ties emissions to the system benefit and cost. This effect, penalize less efficient plants by requiring greater

Lastly, our assessments and comparisons indicate that the clear-cut choices and no panaceas in environmental controls for the future. None of the developing technologies has such an economic advantage. The realities of cost escalation and market competition could not possibly be ignored to negligible proportions. In that case, experience has shown that the industry will opt for what is known best -- existing technology. Particular, utility companies are quite conservative and intrinsically reluctant to accept new technologies with uncertainties in commercial performance and costs. This is not meant to imply that development of new systems should not be undertaken, but only that the performance and potential of each approach must be scrutinized with great care and attention at each stage in its development. Changing priorities, policies, and actions have the power to shift the cost/benefit balance far more quickly than any but the most unusual technological developments.

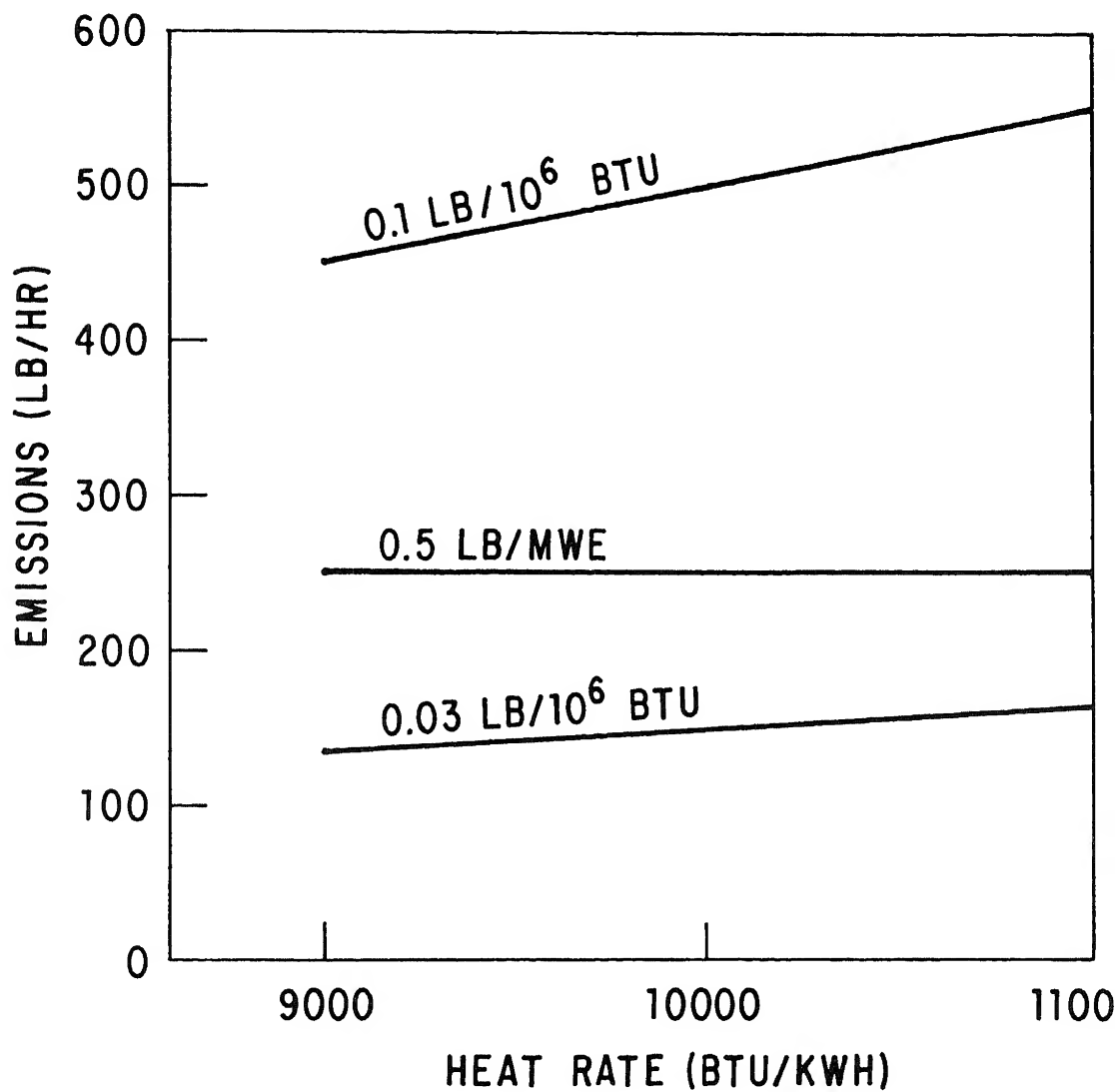


Fig. 6. The Effects of Alternative Regulatory Strategies on Emissions

## 1. INTRODUCTION

Emissions from stationary combustion sources have been effectively reduced to 10% or less of their initial levels for all major air quality criteria pollutants except NO<sub>x</sub>. The conversion of fuel-bound nitrogen to NO during the combustion process makes the control of NO<sub>x</sub> emissions from coal-fired boilers particularly difficult. However, coal is our largest natural fossil fuel source and DOE is responsible for developing methods of utilizing coal in an environmentally acceptable manner. Coal is used extensively for power generation by the electrical utility industry but the increased use of coal in industrial applications cannot be ignored, particularly in air quality control regions where NO<sub>x</sub> air quality standards are barely being met. Consistent with their responsibilities, EPA has established research programs to reduce NO<sub>x</sub> emissions from coal combustion of 200 ppm by 1980 and 100 ppm by 1990. DOE is also currently assembling background technical support documents for the yet-to-be proposed industrial boiler NO<sub>x</sub> emissions regulation.

For the reasons outlined above, a need existed to conduct a comprehensive state-of-the-art review of all potential combustion modification measures for NO<sub>x</sub> control on coal-fired industrial boilers. Combustion modification has been the most cost-effective approach to limiting NO<sub>x</sub> formation in the past. With the resurgence of interest in spreader stoker units, it is desirable to document the most recent technical developments plus R&D needs associated with that boiler design category.

## 2. NO<sub>x</sub> EMISSIONS FROM COAL-FIRED INDUSTRIAL BOILERS

NO<sub>x</sub> is formed during coal combustion from two sources: (1) the thermal fixation of atmospheric oxygen and nitrogen, and (2) the conversion of fuel-bound nitrogen. The availability of oxygen, as well as temperature,

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\*This study was conducted for Argonne National Laboratory under Contract No. 31-108-38-3726 as part of an on-going program, Environmental Control Technologies of Generating Electric Power from Coal, being conducted in the DOE Division of Environmental Control Technology.

ditions. Burner, grate and furnace configurations are important factors in NOx formation since they influence mixing patterns, heat release and absorption rates as well as residence times within the furnace.

Significant variations in firing methods and combustion conditions occur in industrial sized coal-fired boilers. The smaller units (up to approximately 250,000 lb/hr steam flow) are largely stoker-fired units. They differ primarily in the mechanical method of coal introduction into the furnace, including overfed, underfed and spreader stokers. These units are characterized by release and combustion of volatile materials above the grate and bed combustion of the resulting char on the grate. In spreader stokers the coal is hurled into the furnace so that devolatilization and some pre-combustion occurs prior to landing on the grate. In all stokers, the bulk of the combustion air is supplied through the grate.

Larger boilers generally use suspension firing in pulverized or cyclone units. In these units the combustion air is supplied with the coal through individual burners. Several configurations of pulverized-fired units are used. These include tangential, single wall, horizontally opposed and vertical fired boilers. They differ primarily in the location, arrangement and type of burners in the furnace. Other than size and the corresponding number of burners, these boilers are similar in design to utility sized units.

### 3. DEPENDENCE OF NOx EMISSIONS ON BOILER TYPE

NOx emissions from industrial boilers are dependent on the boiler design primarily because variations in the type of combustion influence the conversion of fuel nitrogen. A summary of baseline (or as-found) emissions levels by boiler firing type is presented in Table 1.

Table 1. Summary of Baseline NOx Emission Levels

<u>Firing Type</u>	<u>NOx Emissions, ppm (3% O<sub>2</sub>, Dry)</u>
Suspension Fired	
Cyclone	800
Single Wall	350-900
Horizontally Opposed	500
Tangential	400-500
Vertical	---
Stoker	
Underfed	250-350
Overfed	200-300
Spreader	300-600

to suspension-fired units. The variations in and among stokers and pulverized combustion units is due to the differences in combustion and oxygen availability in the primary combustion regions. The NOx levels from pulverized fired boilers are within the ranges of emissions from small, comparably fired utility boilers (Ref. 1). However, the dependence of industrial boiler NOx emissions on boiler size or capacity is very weak, unlike many coal-fired utility boilers. Typical baseline NOx emissions from industrial boiler capacity for different types of industrial boilers are shown in Table 1 for comparison purposes.

Although industrial boiler NOx emission rates are generally lower than those from utility boilers, considering the stoker emission levels, the total NOx emissions from the industrial category are significant and cannot be neglected in meeting air quality standards. An appreciation for the industrial boiler coal use and annual NOx emissions by boiler type can be gained from Table 2. It should be noted that stoker units represent approximately 80% of total industrial boiler NOx emissions, in spite of their low emission levels relative to those of their large population and fuel use.

Table 2. Estimates of Coal Use and NOx Emissions\*  
From Industrial Watertube Boilers for 1972

	Coal Usage		NOx Emissions	
	$10^{12}$ Btu/Yr	%	$10^3$ TPY	
Pulverized Fired				
Tangential	80.0	4.8	30	
Horizontally Opposed	28.8	1.7	12	
Single Wall	52.8	3.2	21	
Vertical	5.3	0.3	2	
Cyclone	35.0	2.1	28	
(Subtotal)	(201.9)	(12.1)	(93)	(1)
Stoker Fired				
Spreader	641.2	38.3	179	3
Underfed	567.7	34.0	144	2
Overfed	169.6	10.1	53	1
Not Classified	91.2	5.5	25	
(Subtotal)	(1469.7)	(87.9)	(401)	(8)
Total	1671.6		494	

\*Ref. 2

#### 4. COMBUSTION MODIFICATIONS TO REDUCE NOx EMISSIONS

Combustion modifications including low excess air and staged combustion have been effectively used to reduce baseline NOx emissions from industrial boilers.

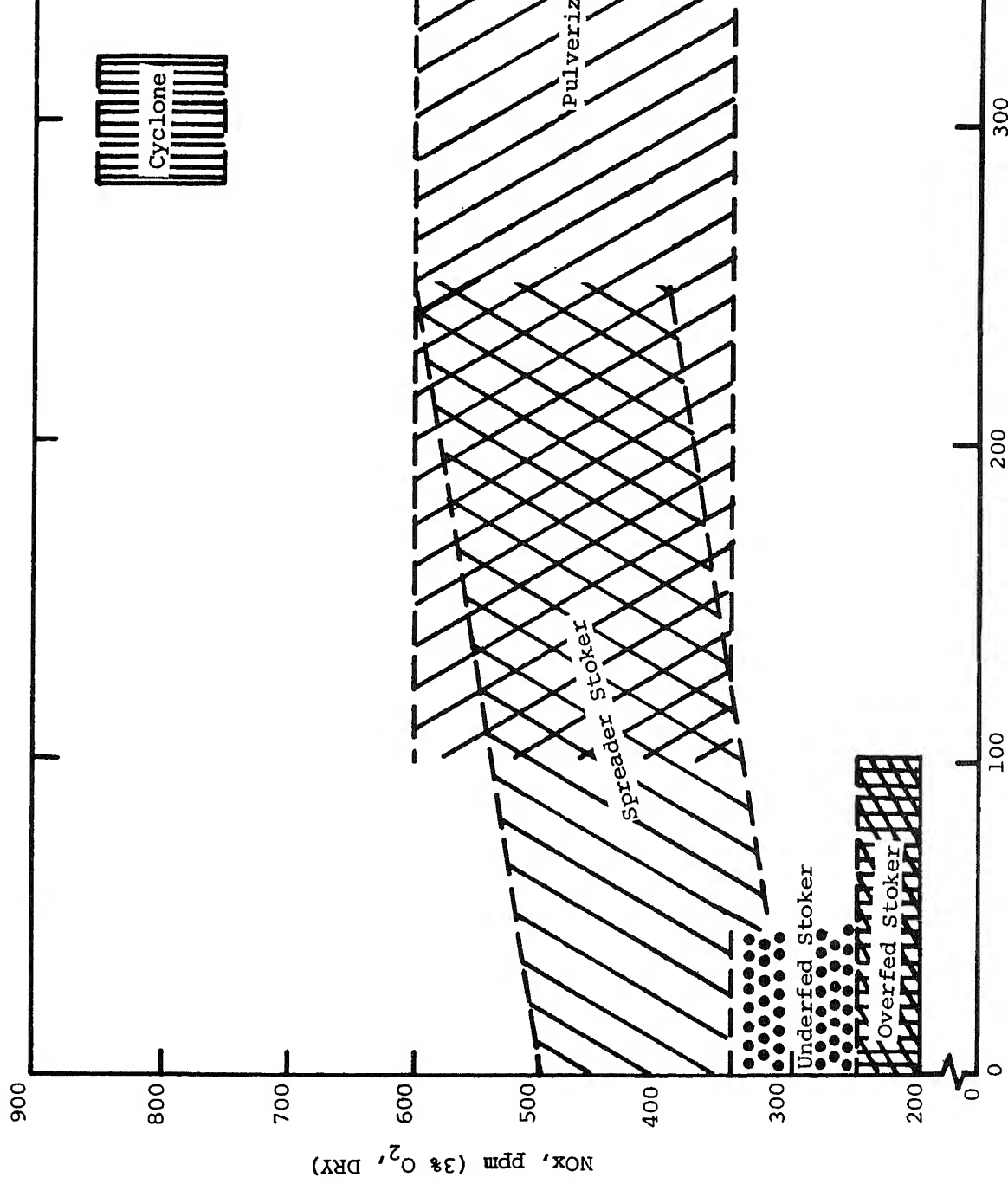


Table 3. Summary of NO<sub>x</sub> Reduction

Firing Type	LEA	Air	BOOS	Simulated	
		Register Adjustment		Injection Systems	Bu
Suspension Firing					
Cyclone	5%	-	-	-	
Single Wall	5 to 10%	15%	30 to 45%		
Tangential	10%	-	40%	-	
Stokers					
Underfed	10%	NA	NA	-	
Overfed	10%	NA	NA	0 to 20%	
Spreader	10 to 15%	NA	NA	0 to 5%	10

NA - Not applicable

Low excess air (LEA) involves operating the boiler with a reduced amount of overall excess air. Minimum excess air levels are determined by factory boiler operating conditions with excessive carbon carryover.

Industrial boilers tend to be operated at various levels (0 to 5% O<sub>2</sub>) above practical smoke limits due to improper air or fuel distribution, equipment limitations, operator/maintenance neglect, etc. The reductions presented in Table 3 apply to a one-percent reduction in excess O<sub>2</sub>. In many instances, the actual reduction potential of LEA (considering the larger available margin in excess O<sub>2</sub>) was greater than the more complex techniques. For spreader stoker units, a reduction in excess air caused a significant reduction in NO<sub>x</sub> as shown in Figure 2. In fact, LEA is the most effective NO<sub>x</sub> control method on existing stoker units.

Staging the combustion process into primary and secondary combustion regions can be achieved through burner-out-of-service (BOOS) and overfire air (OFA) operation. These techniques are very effective in reducing emissions by reducing the availability of oxygen in the primary combustion zones. The application and reduction potential of these techniques are highly dependent on the location and flexibility of the unit's coal supply to the furnace.

BOOS is implemented on pulverized coal-fired units by terminating the flow of coal to selected burners (and thereby increasing coal flow to remaining burners) while maintaining air flow through all burners. In this manner, sufficient segregation of fuel-rich and air-rich zones are created.



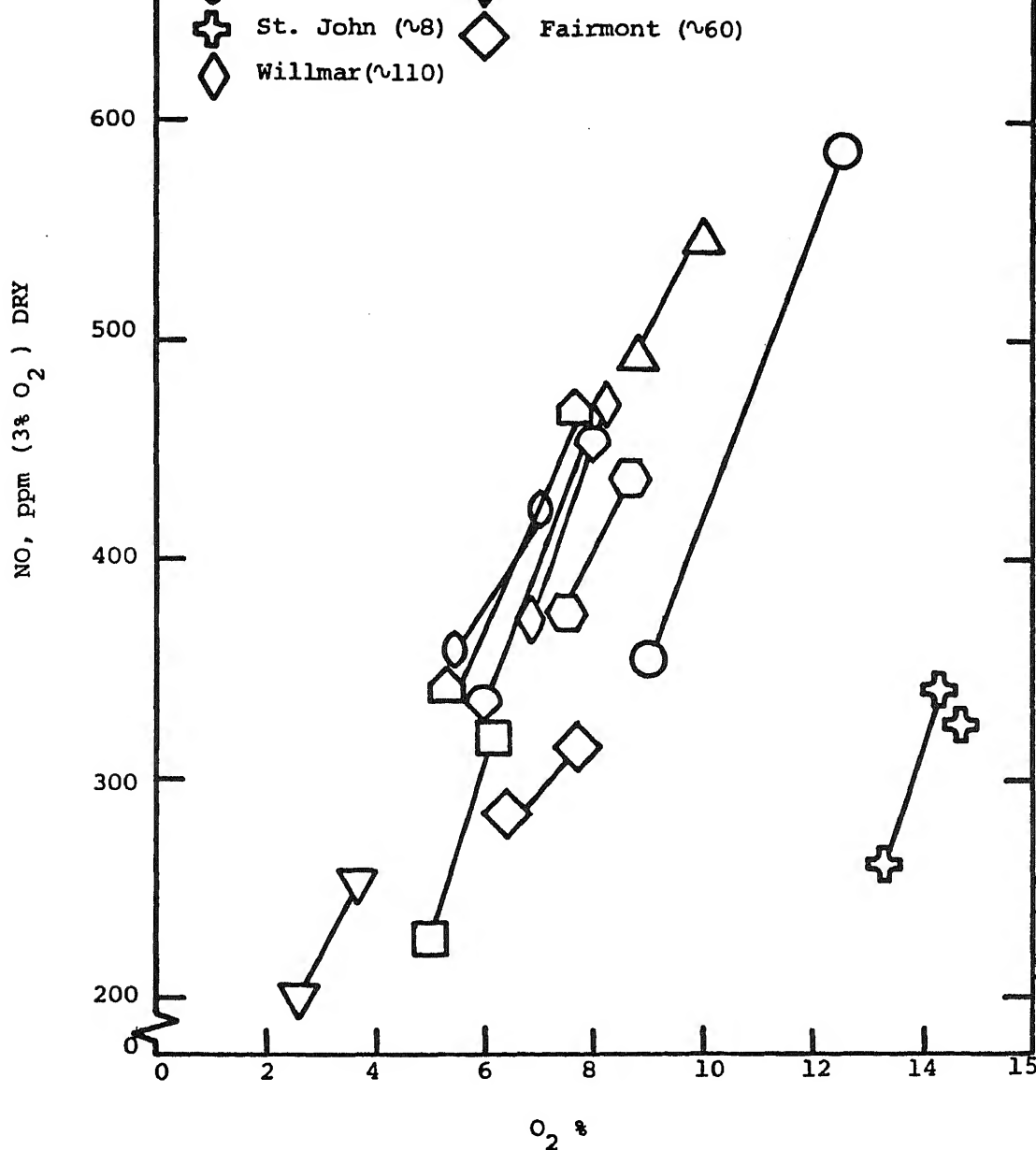


Figure 2. Effect of excess O<sub>2</sub> on NO emissions, spreader stoker units. (Numbers in parentheses indicate operating load in thousands of pounds of steam per hour.)

influence NOx formation the degree of staging (percent of BOOS) which is severely limited on sized units by the few burners involved. Reduction potentials presented in Table 3 represent operation with 25% of the BOOS and reduced loads. This indicates the typical NOx reductions achieved on single wall-fired power coal units. These reduction potentials are comparable to the results on utility sized units with the same degree of staging (Ref. 1). The wide application of BOOS to industrial units is questionable due to load variations unless modifications to burner and coal preparation systems are made.

OFA operation has been simulated on stoker units using both existing overfire air injection systems (installed for increased turbulence in volatile combustion regions directly above the bed) and through the burner systems for auxiliary, wall mounted burners. As given in Table 3, the overfire air injection systems has shown to have little effect on reducing NOx emissions and in fact, increased emissions on an overfired stoker. On auxiliary burners, however, reduced NOx emission levels by 10 to 20%. Test data indicate that optimum design of OFA ports for NOx control could achieve significant reduction potentials on stoker units. Although data on industrial sized suspension fired unit equipped with OFA ports were not available, the results from utility boiler tests showed reduction potentials of 15% and 30% for single wall and tangentially fired units, respectively.

The data presented in this paper were compiled from field test programs conducted by KVB under sponsorship of the EPA and DOE (Refs. 3 and 4). For the most part, the reduction potentials presented in Table 2 were obtained at one load point for short duration tests under steady operating conditions. Examination of these combustion modifications under fluctuating or reduced load conditions over extended periods must be made prior to full implementation as routine operating procedures.

It should also be emphasized that there are large unit-to-unit variations in coal-fired industrial boiler NOx emissions, even within the same boiler design type. This is due to varied boiler geometry with size and coal type. Boiler operating practice, maintenance, coal preparation and coal combustion characteristics often vary from plant to plant even within the same region. Frequently a plant in the northeastern U.S. may obtain coal simultaneously from two or three sources. Therefore, it is unusual to see baseline NOx emissions vary by as much as 400 ppm for the same boiler type. Because of this wide variation in baseline emissions, it is cautioned that the NOx reduction potentials discussed previously cannot be guaranteed for all existing units regardless of boiler age, design type, etc.

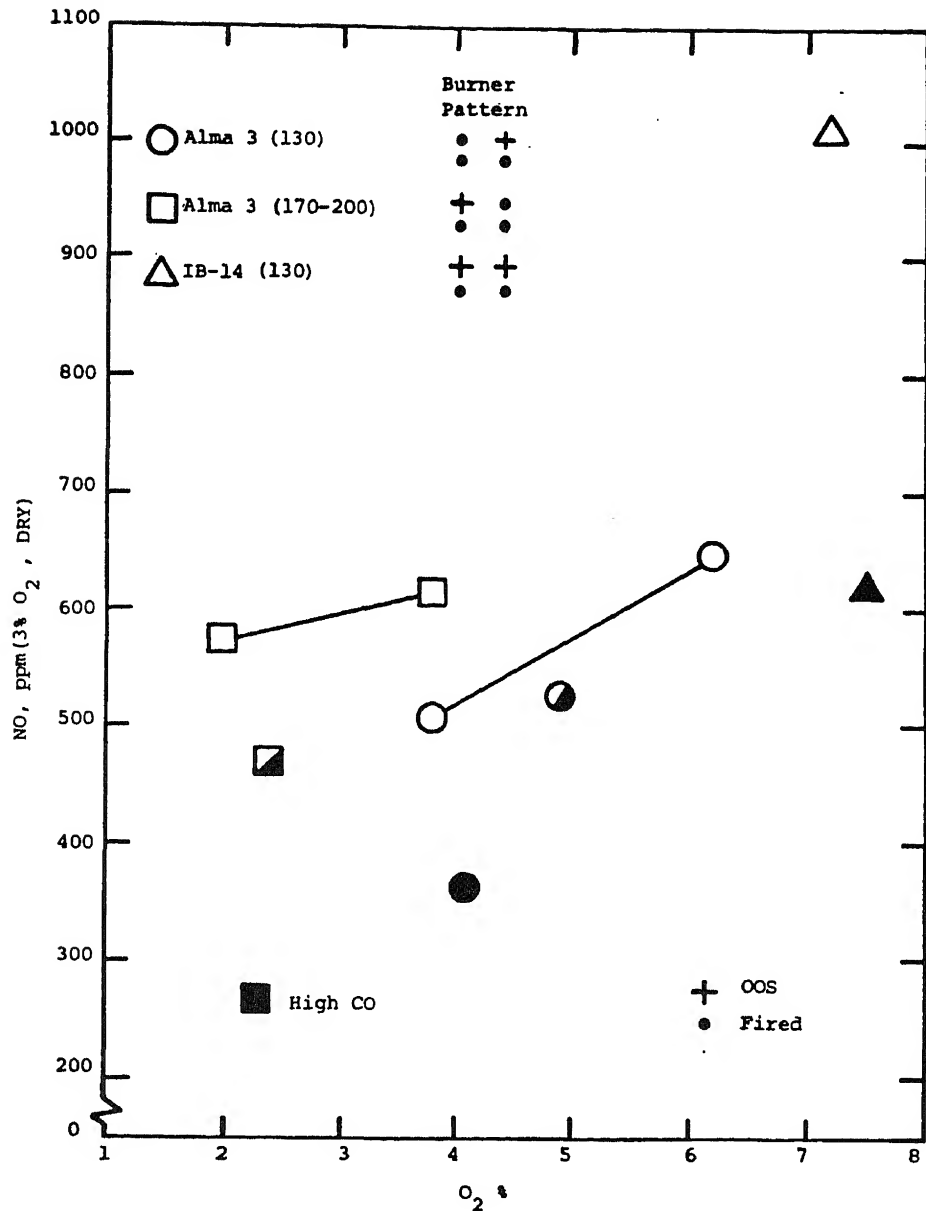


Figure 3. BOOS operation on single wall-fired pulverized coal units for all burners in service (open symbol); no air to BOOS (half shaded symbol); and normal air distribution to the BOOS (completely shaded symbol) (Numbers in parentheses indicate operating load in thousand pounds of steam per hour.)

The impact on boiler operations of the initial and long-term use of staging modifications is, in many respects, as important as the associated NOx reduction potential when considering the use of these techniques. Implementation of procedures that would seriously affect the safety, reliability, or expected life time of these units would be considered unacceptable by boiler owners and operators. Although the implementation of staging techniques on industrial units has been applied only on a test basis, experiences with (1) utility units using BOOS and OFA as normal operating procedures and (2) industrial units operating with LEA for efficiency reasons can give some insight into their possible initial and long term impacts.

Some of the more important concerns and conclusions drawn from a brief review of operational considerations are listed below:

- . The improper application of LEA or staged combustion can result in local reducing conditions that lead to water wall corrosion. This potential problem is being extensively studied on utility boilers by EPA but very little industrial boiler work has been performed.
- . Low NOx emissions require careful attention to boiler maintenance and repair, particularly with regard to burners, combustion controls, and other fuel/air equipment.
- . Improved combustion controls and oxygen analyzers may be required to maintain optimum low NOx operating conditions.
- . Proper implementation of low-NOx boiler operating modes need not necessarily lead to increased fuel use or reduced operating efficiency. In most cases, the improved excess air control offsets the effects of delayed combustion resulting in acceptable CO and particulate emissions at design efficiency.
- . LEA can generally be implemented with a net savings in fuel use whereas advanced staging requires hardware and auxiliary equipment at 0.1 to 0.3% of the total annual cost of operation.

#### 6. ADVANCED CONCEPTS FOR NOx CONTROL FROM COAL-FIRED INDUSTRIAL BOILERS

Advanced staged combustion low-NOx burner/boiler concepts currently developed (Refs. 7,8) for utility boilers have the most promise for pulverized coal industrial boilers. Under government and utility industry sponsorship, NOx emission levels under 100 ppm have been accomplished

eventually multiple burner units.

Advanced NOx control concepts for stokers revolve around the use of overfire air coupled with good undergrate air management to reduce the bed excess air and to lower NOx emissions. Extensive research into controlling NOx emissions from stokers have not been funded but a yet-to-be-awarded EPA program to examine stoker emissions control design options is expected to emphasize NOx control.

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## SUMMARY

The "Low NO<sub>x</sub> Heavy Fuel Combustor Concept Program" is a part of the DOE/LeRC "Advanced Cogeneration Technology Project" (ACT). The program is a contract effort with total funding provided by the Department of Energy, and technical program management provided by NASA LeRC. Main program objectives are to generate and demonstrate the technology required to develop durable gas turbine combustors for utility and industrial applications, which are capable of sustained, environmentally acceptable operation with minimally processed petroleum residual fuels. The program will focus on "dry" reductions of oxides of nitrogen (NO<sub>x</sub>), improved combustor durability and satisfactory combustion of minimally petroleum residual fuels. Other technology advancements sought include: fuel flexibility for operation with petroleum distillates, blends of petroleum distillates and residual fuels, and synfuels (fuel oils derived from coal or shale); acceptable exhaust emissions of carbon monoxide, unburned hydrocarbons, sulfur oxides and smoke; and retrofit capability to existing engines. Development of these capabilities will be accomplished with a minimum and acceptable sacrifice in other combustor performance requirements. Program goals are intended to be optimistic projections of attainable emission reduction and fuel flexibility. The intent is to generate advanced combustor design technology rather than to verify already available technology. Further, it is intended that the generated technology be retrofittable into existing engines in the near-term. The technology generated will be primarily applicable to near-term industrial and utility engines with pressure ratios of 10:1 or higher, which are suitable for cogeneration applications. The technology will also be applicable to future engines.

## INTRODUCTION

This paper describes the Low NO<sub>x</sub> Heavy Fuel Combustor Concept Program including its objectives, program plan, schedule, the basis for its emphasis on heavy oil and synfuels, pollution and performance goals, program approaches to pollution reduction, and status to date.

Limited near and mid-term fuel supplies, as well as competition from other users of natural gas, light and mid-distillates could make it attractive for utility and industrial gas turbine manufacturers and users to fire residual oils in their gas turbine

represents a still more difficult challenge due to their anticipated increase in impurity content, lower hydrogen-carbon ratio and levels of fuel bound nitrogen. Also, under limited circumstances stationary gas turbines may be required to produce ultra-low emissions using presently available clean fuels due to stringent local environmental regulations.

Exhaust emissions from future gas turbines must also meet Federal emission standards. Oxides of nitrogen emission standards are difficult to meet with current light distillate fuel oils, and will become more difficult with residual oils and synfuels. Water or steam injection has been successful in some installations to reduce thermal  $\text{NO}_x$  formation. However, this approach is clearly not a universally acceptable method since it involves considerable additional installation and operational costs, and does not reduce  $\text{NO}_x$  from fuel bound nitrogen. Smoke will also increase with higher fuel firing as a result of lower fuel hydrogen content.

It appears that substantial reduction of pollutants can be attained. The concepts for pollution reduction now exist. However, although the mechanisms of pollution production as well as techniques for reducing pollutants are generally known, application of these techniques to specific combustor-engine designs has not yet demonstrated the anticipated pollutant reductions without compromising other combustor parameters. Thus additional technology is needed to apply these concepts. The Low  $\text{NO}_x$  Heavy Fuel Combustor Concept Program was initiated to provide a timely evolution of combustors.

The program aim is to develop this required pollution reduction technology, apply the technology to combustors for industrial and utility applications, solve interface and performance problems which low pollutant combustor designs create for engine installation, and demonstrate the pollution reductions in steady state and transient testing of development engines.

### PROGRAM DESCRIPTION

#### General

The Low  $\text{NO}_x$  Heavy Fuel Combustor Concept Program is a multi-year contract effort funded by the Department of Energy and administered by the NASA Lewis Research Center. The program's primary objectives are the following:



3. To permit substitution of heavy oils for light distillate fuels and natural gas in the near term.

4. To permit transition to synthetic liquid fuels when they become available.

5. To investigate and develop the technology required to achieve ultra-low emissions (one-half the EPA NO<sub>x</sub> standard) with current clean distillate fuels.

6. To demonstrate the derived technology in full-scale engines.

The program is primarily applicable to near-term industrial and utility engines suitable for cogeneration applications. Additional applicability is desired for future, higher pressure ratio engines.

### Program Plan

It is anticipated that the program will be conducted in three phases. An overall program diagram is contained in Figure 1. Program phases are discussed below:

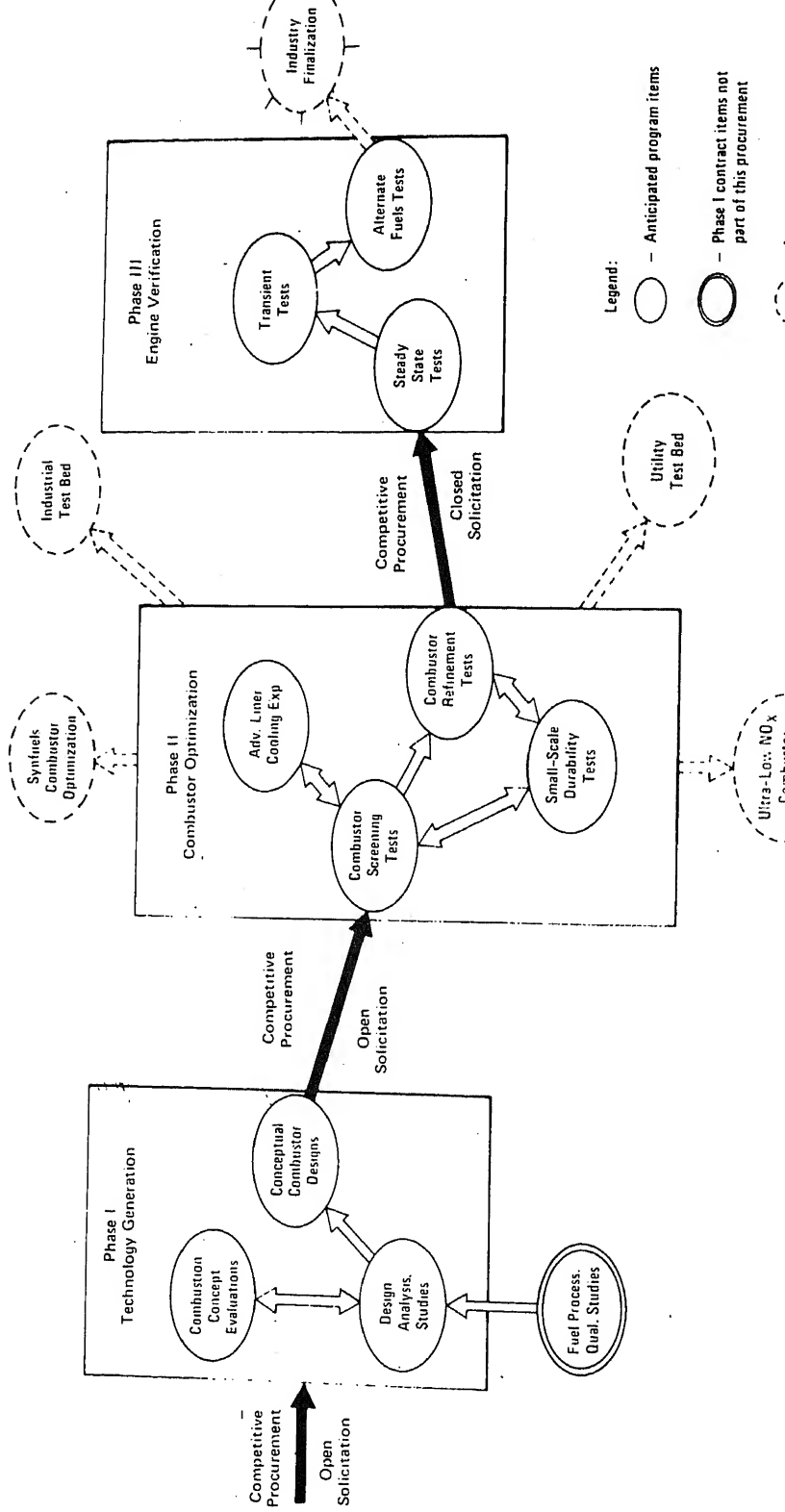
#### Phase I - Combustion Technology Generation

This phase, which is currently in the process of being implemented consists of combustion studies, fuel studies, development of combustion designs, tests, and retests of multiple combustion concepts to determine the best concepts for achieving program objectives. The specific objective of Phase I is to generate the emission reduction and fuels technology required for future program phases. This phase, with the exception of the brief descriptions of Phases II and III presented directly below, is the subject matter of this paper. As with all program phases, Phase I will be a contract effort. Multiple contractors are anticipated.

#### Phase II - Combustor Screening and Optimization

This phase will consist of incorporating the Phase I combustion results into engine-combustor hardware, component testing of promising combustor concepts, iterative redesign and retest of multiple combustor design approaches to determine the best combustor approaches for achieving program goals, and development of combustor liner designs suitable for heavy fuel utilization. The most promising combustor designs will then be tested further to develop the required overall performance, durability and engine adaptability required for engine utilization. Eligible contractors for this phase will not be restricted to those contractors

# Low NO<sub>x</sub> Heavy Fuel Combustor Program



### Phase III - Engine Verification

This phase will consist of evaluating the best combustor(s) of Phase II as part of a complete engine. The intent is to demonstrate in short duration engine testing the emission reductions achieved with fuel flexibility and performance at steady-state and transient conditions. Contractors for this phase will be restricted to those contractors successfully completing the Phase II effort. One or more contractors are visualized.

Since the program emphasizes utilization of minimally processed heavy petroleum fuels, and since burning of petroleum distillate distillate residual blends and synfuels will be assessed but not optimized, the possibility exists for additional program efforts regarding these latter fuels, which are not a part of the current program. Also, if feasible, additional program efforts involving installation of the derived combustors in field engines for extended evaluation may be undertaken. These potential efforts are contained in dashed lines in Figure 1.

### Program Schedule

The planned program schedule is shown in Figure 2. Phase I efforts were initiated in September 1978 with issuance of NASA RFP No. 3-870802. Contract signings are anticipated to occur prior to January 1979, with completion of this phase scheduled to occur within 16 months of contract signing. An approximate 6 month delay is anticipated between the completion of Phase I and the initiation of Phase II, due to procurement procedures. Phase II will be approximately 30 months in duration. It is anticipated that Phase III will be initiated immediately upon completion of Phase II. Phase III will be approximately 16 months in duration.

### Fuels Considerations

#### Fuels availability

Limited near and mid-term petroleum fuel supplies, as well as competition from other users of scarce fuels, could make it attractive for utility and industrial gas turbine manufacturers and users to fire residual oils in their gas turbine equipment. Also, the national goal of reducing dependence on foreign energy supplies in the far-term will make it necessary to use synfuels made from abundant national supplies (Figure 3) of coal and oil shale. Figure 3 also shows the hydrogen to carbon atomic ratio of the various fuel sources. This ratio will be shown in later sections of the paper, to be a major consideration in gas turbine combustor designs. Figure 4 shows the similarity of a heavy

# Proposed Program Schedule

Description	78	79	80	81	82	83	84
Phase I:		<div></div>					
Phase II:				<div></div>	<div></div>		
Phase III:						<div></div>	

**Figure 3**  
**U.S. Remaining Fuel Resources**  
**(Approximate)**

	<u>10<sup>15</sup> BTU</u>	<u>H/C Ratio</u>
Petroleum	700	2.00
Synthetic Fuels*		
Tar Sands	100	1.75
Oil Shale	20,000	1.90
Coal	90,000	0.75
Liquid Fuel Consumption US 40 x 10 <sup>15</sup> BTU/Year		

\*Fossil Fuels Derived from Other than Petroleum

**Figure 4**

# **Liquid Fuels for Directly Fired Engines**

Key Characteristics	Today's Std.		Near-Term Heavy Petroleum		Mid-Term Minimally Processed Coal Der.			
	=2 Distillate	Residuals		*Exxon Donor Solvent	*Light Dist'te.	*H-Coal		I-Ligh Dist'te.
						Heavy Dist'te.	Resid.	
Fuel Bound Nitrogen (Wt. %)	.06		.05 to .5	.7	0.42	1.01	1.3	1.5
Hydrogen/Carbon (Atomic Ratio)	1.8		1.3	1.09	1.38	1.01	1	.8
Ash (Wt. %)	—		.05	.03	Nil	Nil	0.2	0.2
Sulfur (Wt. %)	0.5		0.5 to 2.7	0.6	0.18	0.22	0.48	0.8

feasibility of synfuels. To be economically competitive, synthetic liquids must be minimally processed, i.e., hydrogenation of coal-derived crudes must be kept to an absolute minimum.

### Phase I Test Fuels

Three test fuels have been specified for Phase I. These fuels are described in Table I. Fuel A is a petroleum distillate simulating Diesel #2 properties. The objective of testing with this fuel will be to achieve ultra-low NO<sub>x</sub> which is defined as one half the applicable EPA standard. Ultra-low NO<sub>x</sub> combustors are required in areas where local regulation, more stringent than the EPA standard are in effect.

Fuel B is a petroleum residual fuel and is the major basis for combustion design in this program. Correspondingly, test efforts will emphasize utilization of this fuel. Fuel C is also a petroleum residual, with degraded properties as indicated by the reduced hydrogen-carbon ratio. The intent of testing with this fuel is to simulate operation with synfuels derived from coal or shale. It is anticipated that if available in sufficient quantity, synfuels will be substituted for fuel C during the program.

In addition to testing with the fuels defined above, additional fuel tests will also be conducted in Phase I. Test fuels B and C will be doped with pyridine to investigate combustion approaches for reducing fuel bound nitrogen conversion. Levels up to 0.5% by weight of fuel bound nitrogen will be investigated with fuel B. Levels up to 1.2% by weight of fuel bound nitrogen will be investigated with fuel C.

In addition, blends of fuel A with fuel B, and blends of fuel A with fuel C will also be investigated. The objectives of these tests are: to determine the tradeoffs concerning fuel quality and its effects on combustor emissions and performance.

Several of the difficulties anticipated to be encountered in burning minimally processed heavy fuels are listed in Table II. Increased alkali metal content of heavy fuels are anticipated to create corrosion and deposition problems on combustor liners and turbine blades. Increases in boiling range increase tendencies of gum formation and carbon deposition on fuel nozzles and combustor liners. Reduced hydrogen content causes increased radiation during combustion, thus producing increased heat loading to combustor liners and adversely affecting combustor

<u>COMPOSITION:</u>			
HYDROGEN, WT. %	NMR	12.8 <sup>±</sup> 0.2	10.8 <sup>±</sup> 0.2
SULFUR TOTAL, WT. %	ASTM D129	0.8 max.	0.8 max.
*NITROGEN TOTAL, WT. %	Kjeldahl	0.1 max.	0.2 max.
HYDROCARBON COMPOSITIONAL ANAL.	GCMS	REPORT	REPORT
ASH, WT. %	ASTM D482	20 ppm max.	0.04 max.
ASH MELT TEMPERATURE, °F	TBD	REPORT	REPORT
AROMATICS TYPE:			
AROMATICS TOTAL, VOL. %	ASTM D1319	REPORT	REPORT
SATURATES	TBD	REPORT	REPORT
OLEFINS	TBD	REPORT	REPORT
NAPHTHALENES	TBD	REPORT	REPORT
CARBON RESIDUE:			
ON 10% WT., %	ASTM D524	REPORT	REPORT
ON 100% WT., %	"	REPORT	REPORT
WATER & SEDIMENT, VOL. %	TBD	REPORT	REPORT
<u>VOLATILITY:</u>			
DISTILLATION TEMPERATURE, VOLUME			
RECOVERED, OF --- max.			
INITIAL BOILING POINT	ASTM D86	REPORT	REPORT
10%	"	425 <sup>±</sup> 25	600 <sup>±</sup> 50
50%	"	REPORT	REPORT
FINAL BOILING POINT	"	650 <sup>±</sup> 50	1000 <sup>±</sup> 100
RESIDUE	"	REPORT	REPORT
FLASH POINT, °F	ASTM D93	REPORT	REPORT
GRAVITY, °API	ASTM D287	REPORT	REPORT
<u>FLUIDITY:</u>			
POUR POINT, °F	ASTM D97	20 max.	50 max.
VISCOSITY AT 100 °F:			
KINEMATIC, cS	ASTM D445	REPORT	REPORT
SAYBOLT UNIVERSAL, SEC.	ASTM D88	REPORT	REPORT
<u>COMBUSTION:</u>			
NET HEAT OF COMBUSTION, BTU/LB	ASTM D2382	REPORT	REPORT
<u>THERMAL STABILITY:</u>			
JFTOT, BREAKPOINT TEMPERATURE, °F			
(TDR, 13; ΔP, 25 mm)	ASTM D3241	REPORT	REPORT
<u>TRACE METAL ANALYSIS: ppm</u>			
V	TBD	REPORT	REPORT
Ni	"	REPORT	REPORT
Na	"	REPORT	REPORT
K	"	REPORT	REPORT
Mg	"	REPORT	REPORT
Ca	"	REPORT	REPORT
Pb	"	REPORT	REPORT
Cu	"	REPORT	REPORT
Fe	"	REPORT	REPORT
Si	"	REPORT	REPORT
Zn	"	REPORT	REPORT
Ba	"	REPORT	REPORT
Mn	"	REPORT	REPORT
Mo	"	REPORT	REPORT
Ti	"	REPORT	REPORT

\* Additional Nitrogen concentrations to be investigated are defined in Tasks of Exhibit "A".



# Table II

## Fuel Considerations & Impacts

Parameter	Fuel Types			Effect
	Current # 2	Heavy Oils	High F.B. Nitrogen	
Alkali Metal Content	Low	High	Higher	Corrosion & Deposition
Typical Boiling Range °R	380-650	600-1000	600-1000	Gumming & Carbon Formation
Hydrogen Content Wt. %	12.2-13.2	10-12.5	9-12.5	Luminosity + Smoke
Thermal NO <sub>x</sub>	High for All in Relation to Stds.			
F.B. Nitrogen % Wt.	0-0.2	0-0.5	0.5-1.2	NO <sub>x</sub> Conversion

## Emission Goals

Program emission goals are based on EPA Proposed Regulation, F.R. 40 CFR Part 60 and are subject to all of the constraints and corrections contained in this citation.

The emission goals are contained in Table III. Engine operating conditions for which the goals apply are discussed in a subsequent section. These operating conditions incorporate all engine power levels for load following engine-combustors.

The sulfur dioxide goal represents a limitation on fuel sulfur, since all of the fuel sulfur is transmitted through the combustor. It is included here for consistency with the referenced citation. Subsequent program phases will address the question of fuel sulfur level regarding its removal either upstream or downstream of the combustor. Smoke is not currently regulated by the EPA. Rather, it is subject to local regulation. An S.A.E. number of 20 is consistent with advanced state-of-the-art combustor design practices.

Achievement of the Oxides of nitrogen ( $\text{NO}_x$ ) standard represents the most difficult program goal for achievement. Water or steam injection to reduce oxides of nitrogen by reducing flame temperatures will not be relied upon as a control device in this program. "Dry" reductions of oxide of nitrogen through combustor design will be sought. At present, the technology required to control of  $\text{NO}_x$  through combustor design is not available, even with clean distillate fuels. The current  $\text{NO}_x$  emissions will have to be reduced by a factor of 2 to 3 to meet goals shown in Table III. There are also indications that achievement of the  $\text{NO}_x$  standard value will be more difficult to achieve with heavy fuels. This is shown in Figure 5.

Fuel bound nitrogen levels in the fuel also make achievement of the  $\text{NO}_x$  standard more difficult. Current EPA regulations permit correction for fuel bound nitrogen up to 0.25%. Fuel bound nitrogen levels in excess of 0.25% must be compensated for by reducing the conversion of fuel nitrogen into  $\text{NO}_x$ . Typical fuel bound nitrogen conversion data, for a current production industrial engine are shown in Figure 6.

It is anticipated that additional emission goals will be added to future program phases. For example, a particulate goal is anticipated for program Phases II and III.

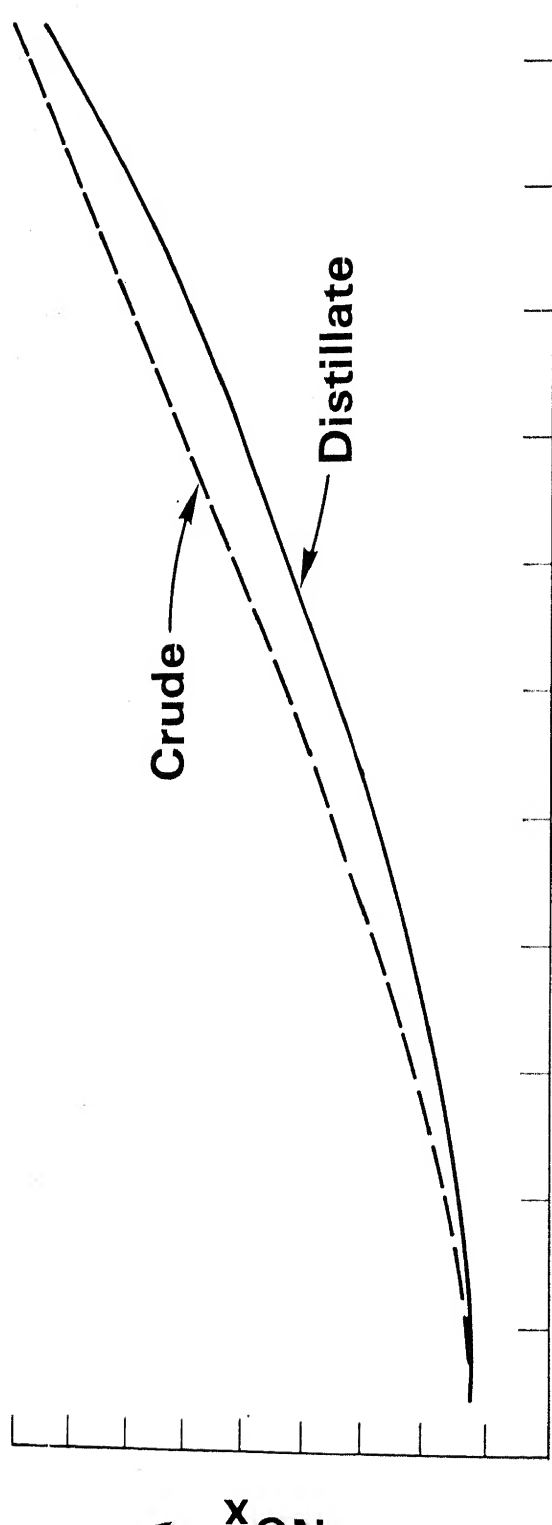
# **Table III** **Emission Goals**

Pollutant	Maximum Level	Operating Cond.
Oxides of Nitrogen <sup>1</sup>	75 PPM @ 15% O <sup>2</sup>	All
Sulfur Dioxide <sup>1,2</sup>	150 PPM @ 15% O <sup>2</sup>	"
Smoke <sup>3</sup>	S.A.E. Number = 20	"

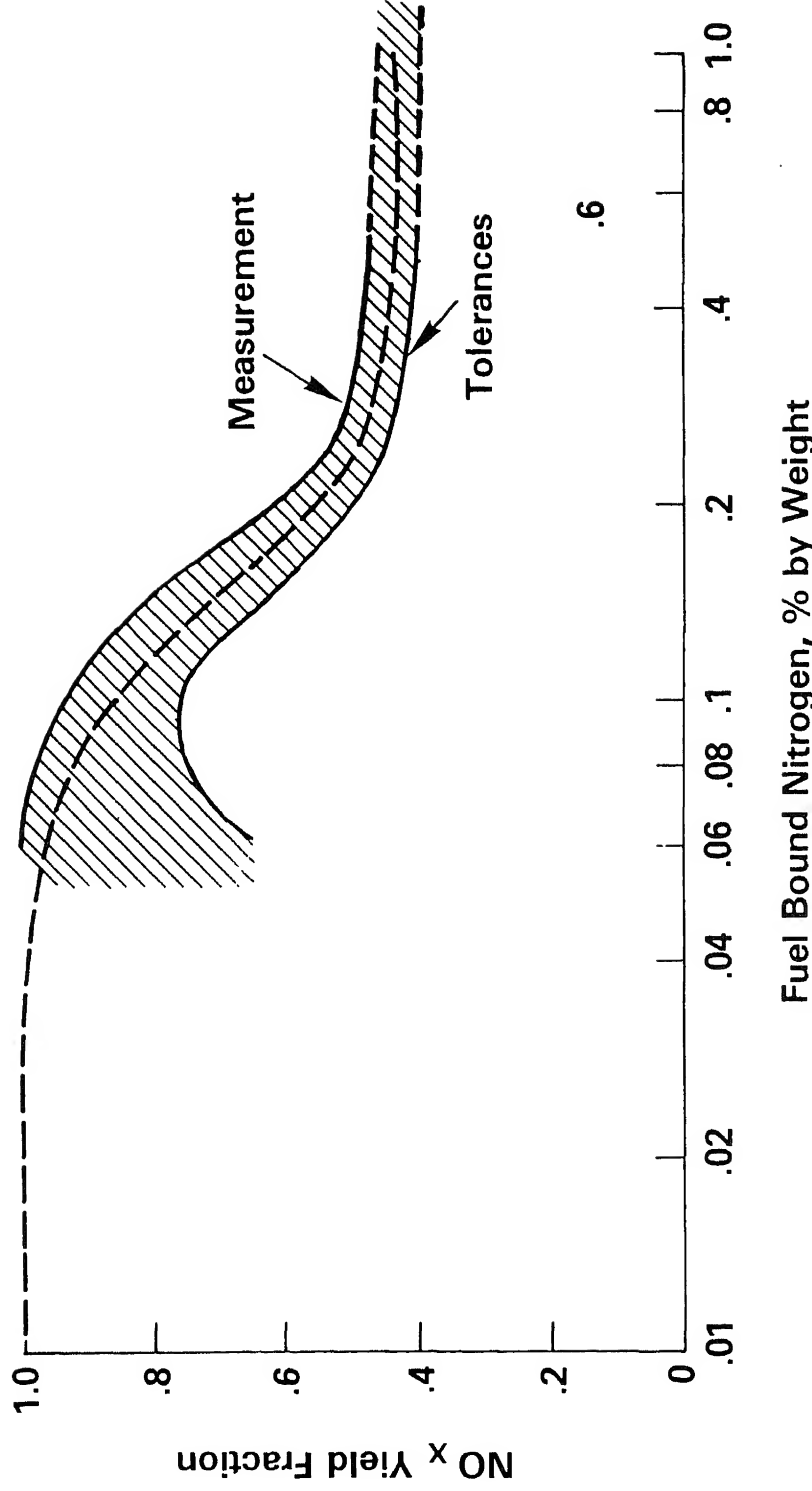
Notes:

- 1 – EPA Proposed Regulation, F.R. 40 CFR Part 60
- 1,2 – Limit of Fuel Sulfur Content
- 3 – No EPA Regulation, Local Rules

**Figure 5**  
**Thermal NO<sub>x</sub> Considerations**  
**Typical Combustor**



**Figure 6**  
**Fuel Bound NO<sub>x</sub> Considerations**



The combustion efficiency goal effectively imposes maximum allowable levels of unburned hydrocarbon (HC) and carbon monoxide (CO), since levels of these emissions are directly related to combustion inefficiency. Conversely, program measurements of combustion efficiency are specified to be recorded through emission level determinations. Current combustors operate very efficiently at high engine power points (50% of engine rated power level and above). However at lower engine power levels, especially at spinning idle conditions, combustion inefficiencies occur with most current engines.

### Test Conditions

Combustor test conditions over which the emission and performance goals apply are contained in Table V. Implicit in the selection of these test conditions is a requirement for load following capability. Load following capabilities are deemed to be necessary for this program because cogeneration applications for the derived technology are visualized. Most industrial and utility gas turbine engine combustors operate efficiently at a nominal base load condition and somewhat less efficiently at off-design or lower power conditions. The requirement that engine combustors operate efficiently over a load range is a significant requirement. To achieve this type of operation, combustor performance must be optimized for a variety of combustor inlet conditions, including those of low temperature, pressure and fuel/air ratio.

### Combustor Considerations and Design

Advanced combustor designs will be emphasized in the Phase I program. A non-inclusive list of pollution reduction techniques which will be investigated in the program are contained in Table VI. Included in the table is the pollutant of concern and the corresponding pollution reduction concept.

Control of thermal  $\text{NO}_x$  involves reduction of flame temperatures below 3000°F and short residence times of combustion gases at high temperatures. Simultaneous control of thermal  $\text{NO}_x$  and smoke additionally requires uniform distribution of fuel and air, and avoidance of excessively high fuel rich zones. Control of the conversion of fuel bound nitrogen into  $\text{NO}_x$  involves burning under fuel rich conditions or, correspondingly, oxygen lean conditions.

The technology developed in Phase I should be applicable to all types of gas turbine combustors. An illustration of these

# **Table IV** **Performance Goals**

Combustion Efficiency*	>	99% at All Operating Conditions
Total Pressure Loss	<	6% at Base Power Load
Outlet Temperature Pattern Factor	=	0.25 at Base Load & Peak Load Power
Combustor Exit Radial Temperature Profile	=	Equivalent to Production Comb. Values

\*Calculated on a Deficit Basis from Measurements of Co, THC & Co<sub>2</sub>

# Table V

## Proposed Combustor Test Conditions

Cold Start

Spinning Idle

30% Rated Power

50% Rated Power

70% Rated Power

80% Rated Power — Nominal Base Load Condition

100% Rated Power — Peak Load Condition

Parametric Variation



**Table VI**

**Pollution Reduction Techniques**

Pollutant	Reduction Concept
Thermal NO <sub>x</sub> Reduction	Diluent Injection into Burning Zone Quick Quench Catalytic Combustion
Thermal NO <sub>x</sub> and Smoke Reduction	Premixed/Prevaporized Burning
	Ultra Lean Burning
	Advanced Fuel Injection
	Multiple Fuel Utilization
Organic NO <sub>x</sub> Conversion Reduction	Rich Burning with Controlled Quench

Multi-zone combustors represent advanced technology which is currently being evolved for both ground based and aircraft gas turbine combustors. Multi-zone designs, while considerably more complex than current designs, provide additional degrees of flexibility in staging fuel and combustion to optimize performance for a variety of test fuels, emission and performance constraints.

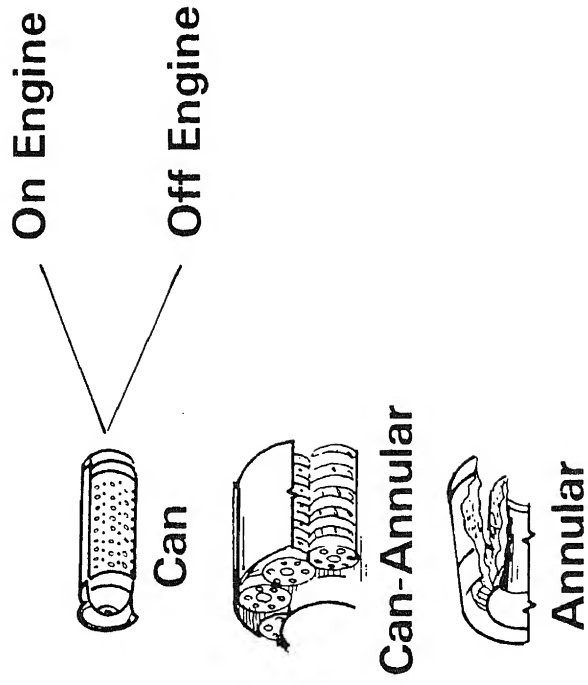
#### CONCLUDING REMARKS

It is anticipated that Phase I of this program will provide the technology base for future program phases. Specifically it is anticipated that Phase I will provide the following:

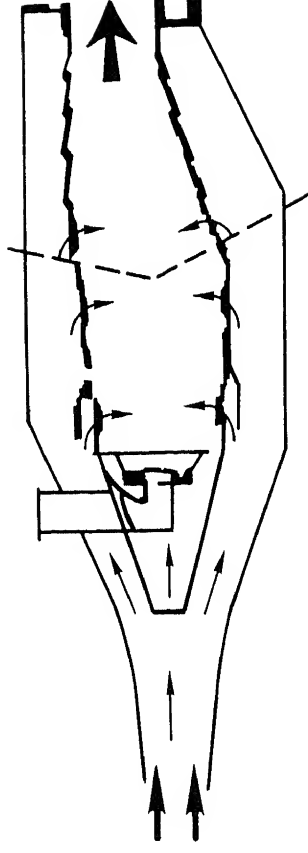
1. Definition of the most promising combustor design approaches for utilizing heavy fuels derived from petroleum and other sources.
2. Definition of tradeoffs involving fuel quality and combustion and emission performance.
3. Identification of realistic fuels for future program phases.
4. Identification of engine applications for the derived technology. This will include preparation of conceptual engine combustor designs.
5. Identification of development efforts required to utilize minimally processed heavy fuels in sub-component combustor areas such as fuel systems, liners, etc.

# Figure 7

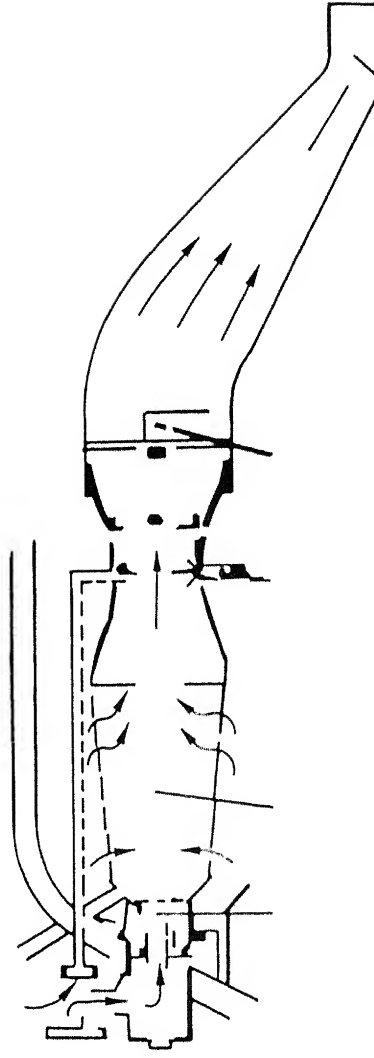
## Potential Combustor Types



# Combustor Designs



Single-stage



Multi-zone

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### ABSTRACT

Midwest Research Institute conducted a project under contract with Argonne National Laboratory to assess the economic and energy impacts of particulate control systems in coal-fired power plants. The assessment was based on major functional variables such as plant size (100 to 1,000 MWe), location, coal type, and emission standards. The work resulted in the generation of algorithms to predict equipment cost, installation costs, and energy usage for various particulate control devices. The devices considered were: electrostatic precipitators (hot-side and cold-side); fabric filters (reverse air and shake types); and wet scrubbers.

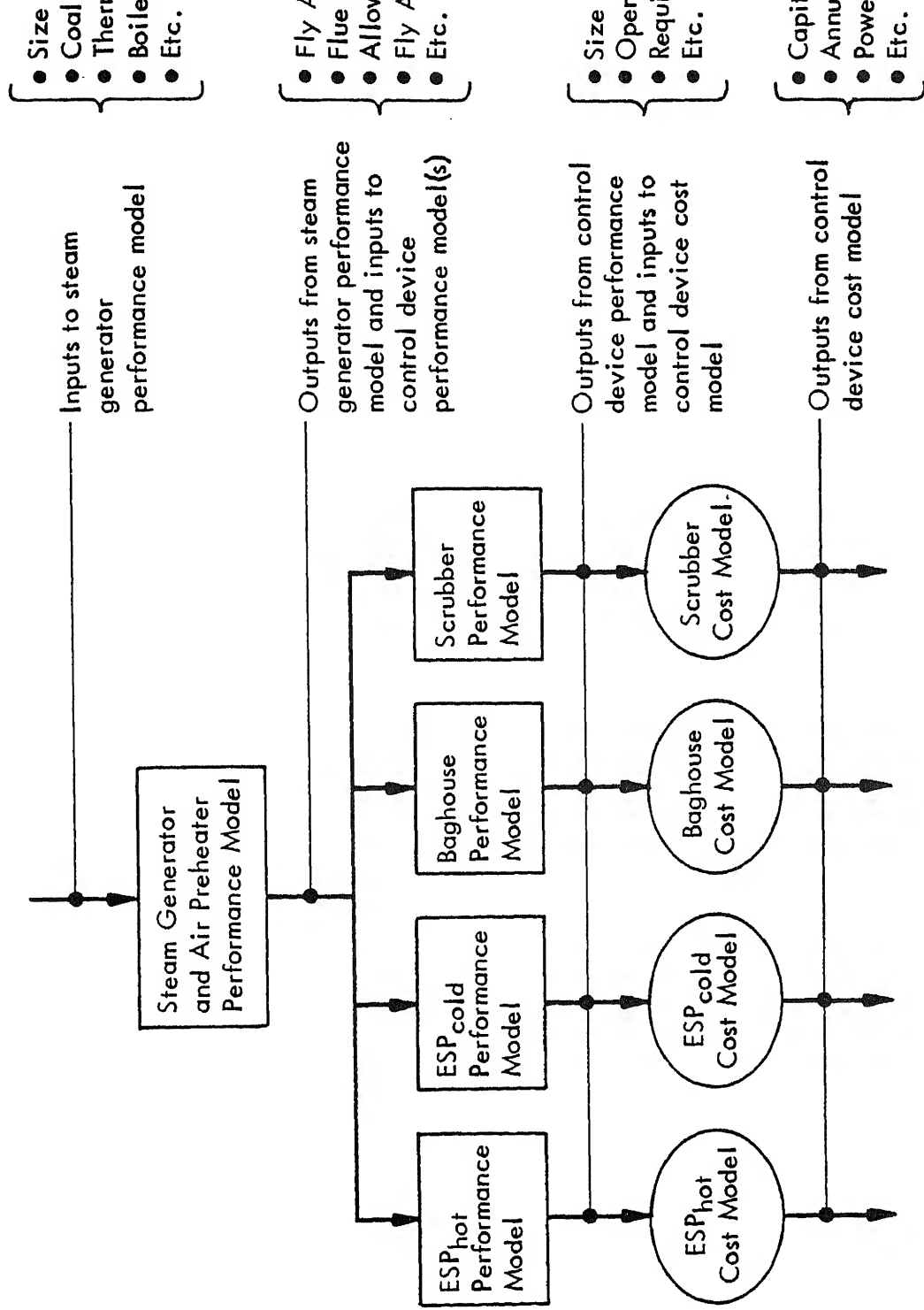
A boiler performance model was developed using variables such as plant size, coal characteristics, etc. The output from this model (i.e., flue gas flow rate, grain loading, etc.) was utilized in control device performance models to generate required design and operating parameters for the control systems under study. The design and operating parameters were then used in the cost models that were also developed in this program.

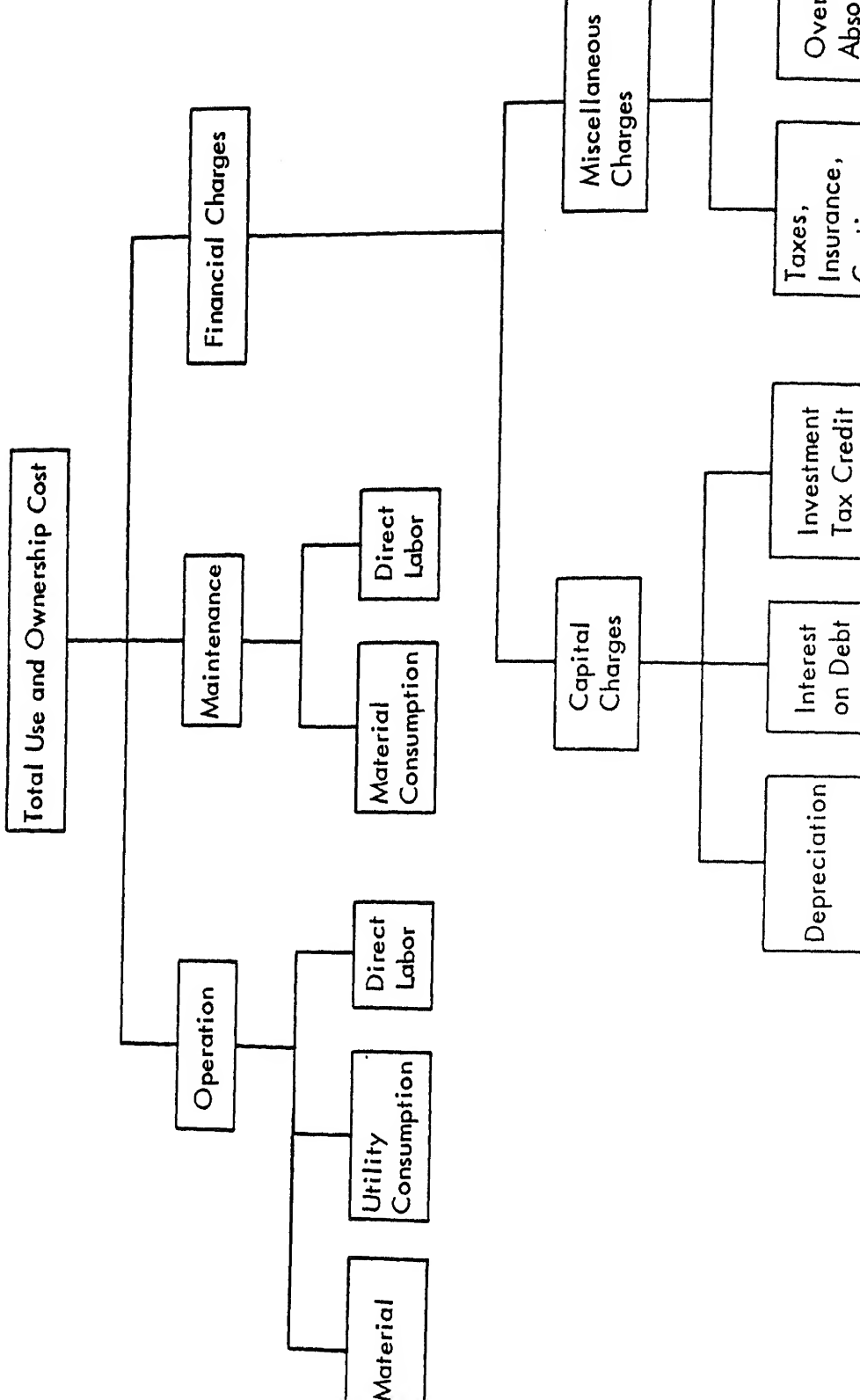
The cost models aggregate three cost items: (a) the first-year costs (capital investment); (b) total first-year annualized costs; and (c) the integrated cost of ownership and operation of the control equipment over an assumed plant lifetime of 30 years. The models have been programmed for speedy computation. However, the algorithms are easily solvable with a hand calculator. In addition, suitable guideline values have been provided for independent variables wherever necessary. Case studies are presented to demonstrate results of the models.

0.03 lb/10<sup>6</sup> Btu). Since there are a number of control options available for particulate control, there is a need for being able to estimate the economic and energy impacts of each control option for a given set of plant specifications. Realizing this need, Argonne National Laboratory contracted with Midwest Research Institute (MRI) to develop the necessary algorithms to predict equipment cost, installation costs, and energy usage for five particulate control devices: electrostatic precipitators (ESPs) including hot-side and cold-side, fabric filters, both reverse air and shaker type, and wet scrubbers.

The methodology used for the model development is presented in Figure 1. A set of algorithms was developed to quantify the effect of a boiler that relate to the design of fly ash control equipment. This boiler performance model utilizes input values such as plant size, coal characteristics, and boiler type for the computation of parameters critical to control devices (e.g., flue gas flow rate, uncontrolled particulate emissions, etc.). Thereafter, algorithms were developed that use the information generated by the boiler performance model plus the emission limit specified, to compute various control device design parameters (e.g., collecting area for an ESP). A subsequent set of algorithms use these device parameters to compute equipment and operating costs and energy usage. The breakdown of cost items considered is presented in Figure 2. The cost and performance algorithms discussed in this paper are composites of relationships published in the literature and additional information obtained as part of this project.

The following sections of this paper describe the salient features of the boiler performance model as well as the control device performance and cost models, including the various cost and energy consumption factors that were considered. The final section presents a summary of the results obtained from these models when applied to a hypothetical 500-MWe plant at three different geographic locations burning three different coals.







suggested default values are given. This procedure is also followed for many of the other algorithms developed in this project.

Table 1. Steam Generator Performance Model Inputs

Description	Unit	Default Value
Generation rate	MWe	-
Boiler type	-	-
Pulverized coal dry bottom or wet bottom, or cyclone		
Plant location, state	-	-
Heating value of coal	Btu/lb	-
Plant thermal efficiency, decimal fraction	-	0.388
Flue gas temperature	°F	
At preheater inlet		700
At preheater outlet		350
Boiler emission factor	lb fly ash/lb of ash in coal	
For pulverized coal dry bottom boiler		0.85
For pulverized coal wet bottom boiler		0.65
For cyclone boiler		0.10
Excess combustion air, decimal fraction	-	
For pulverized coal boilers		0.20
For cyclone boilers		0.15
Coal analysis, decimal fraction for N, C, H, S, and H <sub>2</sub> O	-	-

- . Coal firing rate, tons/hr,
- . Flue gas flow rate, acfm,
- . Heat input rate,  $10^6$  Btu/hr,
- . Mean diameter and standard deviation of fly ash particle size distribution, and
- .  $\text{SO}_2$  flow rate in flue gas, lb/min.

The above parameters then constitute the inputs to the various control device design models.

Before describing the control device design and cost models on an individual basis, several aspects that the models have in common are identified.

First, the algorithms generate costs in 1978 dollars, but provisions have been made for the user to modify the costs to any year dollars beyond 1978 by using projected cost indices.

Second, a table is provided in the original report<sup>1/</sup> that allows for state-to-state variations in costs, including wage rates, power costs, construction costs, and land acquisition costs. In the cost models, which may be adjusted for different locations, an average wage of \$7.41/hr was used for utility workers and an average land cost of \$10,000/acre.

Third, the cost of the control devices was amortized on an accelerated basis over a 5-year period, per the Tax Reform Act of 1986. Interest was assumed to be 8%, based on the prime rate, but the user may specify other values. Also, an investment tax credit of 10% was applied for the first year of operation.

Fourth, one of the cost criteria used in the overall economic analysis was the total cost of owning and operating the plant over a specified plant lifetime (e.g., 30 years) in terms of first-year dollars. This computation requires several economic projection figures including discount rates for present value analysis and increases in

report.

The performance and cost models developed for each control device contain several algorithms. The following sections discuss the more important ones and their development.

#### A. Cold-Side ESP

1. Performance model: The familiar Deutsch equation was used for "sizing" a cold ESP. This equation requires knowing the particle migration velocity, so a modified form of algorithm developed by Southern Research Institute (SRI)<sup>2/</sup> was used which computes the migration velocity parameter as a function of:

- . Type of boiler,
- . Current density,
- . Power density,
- . Voltage,
- . Number of electrical sets,
- . Moisture content of flue gas,
- . Sulfur and ash in coal,
- . Flue gas temperature, and
- . Uncontrolled fly ash loading.

Since all of the above variables may not be known by the user, suggested default values are given, some of which are selected on the basis of the sulfur content of the fuel.

The Deutsch equation uses the migration velocity along with the gas flow rate and the required collection efficiency to compute the collecting area. The collecting area then becomes a major input parameter for the ESP cost model.

2. Cost model: Equipment and installation costs for the cold ESP are computed using algorithms developed from a model by Bubenick<sup>3/</sup> and data reported by the Industrial Gas Cleaning Institute (IGCI).<sup>4/</sup> The following equations result for equipment and installation costs:

$$EC_C = 45.94 A_{CP}^{0.88}$$

$$IC_C = 23.58 \cdot ACF \cdot A_{CP}^{0.896}$$

$A_{CP}$  = collecting plate area,  $\text{ft}^2$

ACF = area construction factor

The cost model also contains several other cost algorithms for computing:

- . Ash handling equipment cost,
- . Ash handling installation cost,
- . Land cost,
- . Electrical capacity charge,
- . Power cost,
- . Operating labor cost,
- . Maintenance material cost, and
- . Maintenance labor cost.

The electrical capacity charge in the above list represents the cost of additional power plant capacity that is required to meet the electrical requirements of the control device. The value used is \$900/kw.

In addition to the financial charges discussed earlier (depreciation and investment tax credit), the cost models also include taxes, insurance, and contingency.

## B. Hot-Side ESP

1. Performance model: The hot-side ESP model also uses the Deutsch equation for computing the collecting plate area. If available data on hot ESP were not sufficient to develop an algorithm for migration velocity, the user must specify a migration velocity. To select one of the suggested default values, which are as follows:

0.30 ft/sec for pulverized coal boiler burning coal with  
> 1% sulfur

0.25 ft/sec for pulverized coal boiler burning coal with  
< 1% sulfur

0.18 ft/sec for cyclone boiler

where:

$EC_H$  = hot ESP equipment cost, 1978 dollars

$IC_H$  = hot ESP installation cost, 1978 dollars

$A_{HP}$  = collecting plate area,  $ft^2$

ACF = area construction factor

Algorithms were also developed for other cost items listed above. These algorithms are similar in form to those for the cold ESP however, one additional factor included for the hot ESP is heat loss from the ESP due to higher operating temperature. It was assumed that this heat loss results in additional fuel consumption to maintain the power output. Since data collected in this project indicated that the average drop in the flue gas temperature across a hot ESP is about 79°F, this was the value used in an algorithm to compute the annual cost for the additional fuel. The cost of the fuel is based on a default value of \$1.75/10<sup>6</sup> Btu. The annual cost of this heat loss is a significant portion of the total annual operating cost for a hot ESP.

### C. Fabric Filters

1. Performance model: Performance and cost models were developed for both reverse flow and shaker type baghouses, the costs based primarily on cloth area required. This parameter is calculated in the performance models using an air-to-cloth ratio specified by the user, or a default value of 2.0 acfm/ $ft^2$  for reverse flow type and 2.0 acfm/ $ft^2$  for shaker type. These are net values, allowing for one compartment being off-line for cleaning and one off-line for maintenance.

The pressure drop through baghouses is considerably higher than in ESPs, and it significantly affects operating costs. Therefore algorithms were developed to compute the pressure drop using information from baghouse manufacturers and the recent TVA/Shawnee project.<sup>5/</sup>

$$EC_{RB} = 16.6 \text{ GCA}$$

$$EC_{SB} = 21.08 \text{ GCA}^{0.966}$$

where:

$EC_{RB}$  = equipment cost, reverse flow baghouse, 1978 dollars

$EC_{SB}$  = equipment cost, shaker baghouse, 1978 dollars

$GCA$  = gross cloth area,  $\text{ft}^2$

Gross cloth area is also the major parameter used in estimating installation costs for the baghouses. Many of the other operating costs are similar to the ESP model. But an additional item considered for the baghouses was bag replacement. Average bag replacement costs were used to develop the following equation for this cost item:

$$RBC_{RB} = 0.78 \text{ GCA}$$

$$RBC_{SB} = 0.63 \text{ GCA}$$

where:

$RBC_{RB}$  = cost of replacement bags, reverse flow baghouse, 1978 dollars

$RBC_{SB}$  = cost of replacement bags, shaker baghouse, 1978 dollars

$GCA$  = gross cloth area,  $\text{ft}^2$

It was assumed in the default condition that all bags be replaced every 3 years, although the user may specify otherwise. Additionally, equations were developed for bag replacement costs.

The algorithms developed for the financial charges are similar to those for ESP.

1. Performance model: The model developed (for venturi scrubbers) considers fly ash removal only and excludes those scrubber systems in which particulate and  $\text{SO}_x$  control are achieved simultaneously. (However, it does consider the neutralization requirements due to the absorption of certain amounts of  $\text{SO}_x$ .) Development of the scrubber performance model was based on work by Calvert<sup>6,7,8/</sup> and involves a trial and error procedure to determine the pressure drop and liquid-to-gas ratio required. Several simplifying assumptions were made in developing the design equations. Some of these assumptions relate to the specific application area of the model, viz., fly ash control in coal-fired boilers.

2. Cost model: Total equipment cost for the venturi scrubber was derived from costs reported in the literature. Regression analysis indicated that these data can best be expressed by:

$$\text{EC}_S = 1.59 Q_S^{1.062}$$

where:

$\text{EC}_S$  = equipment cost, scrubber, 1978 dollars

$Q_S$  = saturated flue gas flow rate, acfm

Several other cost algorithms were developed to determine:

- . Installation cost,
- . Land cost (for the scrubber and for a settling pond),
- . Power usage,
- . Electrical capacity charge,
- . Operating labor cost,
- . Material cost (lime and water),
- . Maintenance material,
- . Maintenance labor, and
- . Flue gas reheat cost.

Like the hot ESP heat loss, the flue gas reheat is an additional cost associated with wet scrubbers. An algorithm was developed to calculate the cost for equivalent fuel. The algorithm assumes an energy cost of  $\$1.75/10^6$  Btu and a reheat requirement of 50°F, unless the user specifies otherwise.

This model also includes all the financial charges discussed

case studies. The input parameters were used in the calculations for the three case studies shown in Table 2. These input parameters were used in the calculations for the three case studies to derive design and/or size specifications for the control devices based on the models described in the early studies (Table 3).

Table 4 presents the cost comparisons for the control devices resulting from the calculations for the three case studies. Table 4 shows that the relationship of cost factors for the different control devices is the same; i.e., for any single case, the cost ranking of the devices is the same regardless of which cost factor is used. It is found that the cold ESP is the least expensive control method for the cases of medium and high sulfur coal. In the case of low sulfur coal, however, the cold ESP is shown to be more expensive than a hot ESP or either of the baghouses. Comparing the hot ESP and baghouse, the former is more effective for low sulfur coal. In medium and high sulfur coal cases, the hot ESP is more expensive than the cold ESP but less expensive than either of the baghouses. The cost of the baghouse remains fairly independent of coal characteristics. Clearly, the high operating equipment cost of scrubbers make them uneconomical if they are used only for particulate control.

A comparison of energy consumption factors for different control devices is presented in Table 5. In terms of total energy consumption, the results show that a cold ESP ranks as the most energy efficient device, followed by a baghouse and then a hot ESP. Particulate control devices are shown to be the highest energy consumers. From the data in Table 5, it is evident that the high energy consumption of scrubbers is due, in part, to stack gas reheat and heat losses. For example, in the case of a scrubber with Pennsylvania coal, 10.1 Btu/lb of energy are required for stack gas reheat in comparison to 1.1 Btu/lb of energy for the operation of the scrubber.



Table 2. Fundamental System Characteristics of Sample Gases

System Characteristic Items	Sample Case 1	Sample Case 2	Sample Case 3
Plant site (mine-mouth plant)	Rosebud County, Montana	Franklin County, Illinois	Westmoreland County, Pennsylvania
Coal source	Rosebud County, Montana	Franklin County, Illinois	Westmoreland County, Pennsylvania
Coal cleaning	Level 1	Level 1	Level 1
Coal characteristics <sup>a</sup>			
Moisture	13.6	4.10	5.0
Ash	7.6	7.20	22.0
Sulfur	0.60	2.58	3.23
Carbon	60.00	72.30	60.00
Hydrogen	5.4	5.4	5.4
Nitrogen	1.6	1.6	1.6
Heating value, Btu/lb	10,116	12,768	10,912
Regulations	New Source Performance Standards (NSPS), i.e., 0.03 lb/10 <sup>6</sup> Btu	New Source Performance Standards (NSPS), i.e., 0.03 lb/10 <sup>6</sup> Btu	New Source Performance Standards (NSPS), i.e., 0.03 lb/10 <sup>6</sup> Btu
Boiler type	Pulverized coal-fired dry bottom boiler	Pulverized coal-fired dry bottom boiler	Pulverized coal-fired dry bottom boiler
Capacity <sup>b</sup>	500 MWe total	500 MWe total	500 MWe total

<sup>a</sup>Weight percent as received.

<sup>b</sup>The power consumed internally for the operation of the control equipment is not considered.

Low Sulfur Montana Rosebud Coal (Case 1)

Migration velocity, ft/sec	0.110	0.25	-	-
Collecting plate area, ft <sup>2</sup>	1,330,281	840,966	-	-
Specific collector area, ft <sup>3</sup> /1,000 acfm	811	513	-	-
Gross cloth area, ft <sup>2</sup>	-	-	956,595	683,282
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft <sup>3</sup>	-	-	-	-

Medium Sulfur Illinois No. 6 Coal (Case 2)<sup>b</sup>

Migration velocity, ft/sec	0.418	0.30	-	-
Collecting plate area, ft <sup>2</sup>	307,336	613,733	-	-
Specific collector area, ft <sup>3</sup> /1,000 acfm	203	282	-	-
Gross cloth area, ft <sup>2</sup>	-	-	885,112	632,223
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft <sup>3</sup>	-	-	-	-

High Sulfur Pennsylvania Coal (Case 3)<sup>c</sup>

Migration velocity, ft/sec	0.386 <sup>d</sup>	0.30	-	-
Collecting plate area, ft <sup>2</sup>	428,971	789,979	-	-
Specific collector area, ft <sup>3</sup> /1,000 acfm	275	354	-	-
Gross cloth area, ft <sup>2</sup>	-	-	909,328	649,259
Pressure drop, in. WG	1.0	1.0	4.72	3.73
Liquid-to-gas vol. flow rate ratio, gal/1,000 ft <sup>3</sup>	-	-	-	-

<sup>a</sup>Required particulate collection efficiency per the proposed NSPS of 0.03 lb/10<sup>6</sup> Btu: 99.5%

<sup>b</sup>Required particulate collection efficiency per the proposed NSPS of 0.03 lb/10<sup>6</sup> Btu: 99.4%

<sup>c</sup>Required particulate collection efficiency per the proposed NSPS of 0.03 lb/10<sup>6</sup> Btu: 99.3%

<sup>d</sup>Migration velocity is lower than for medium sulfur case due to the high ash content of coal

Table 4. Particulate Control Cost Analysis

Control Device	Total Installed Cost <sup>a</sup> (1978 dollars)	Total Installed Cost <sup>a</sup> and Inst. Elec. Capacity Charge (1978 dollars)	Aggregate Cost of Ownership and Operation Over 30 Years (1978 dollars)	Total Annualized Cost of Operation <sup>b</sup> 1978		Annual Opera and Maint 1978 dollars
				dollars	Mills/kWh <sup>c</sup>	
<u>Low Sulfur Montana Rosebud Coal (Case 1)</u>						
Cold-side ESP	18,633,567	19,209,238	72,947,000	6,604,946	1.7755	220,642
Hot-side ESP	11,214,934	12,623,368	60,038,000	4,416,378	1.1872	423,124
Reverse flow baghouse	15,605,788	17,969,442	141,987,000	7,921,770	2.1295	1,397,052
Collapse + shake bag- house	14,645,403	16,718,784	126,029,000	7,033,680	1.8908	981,507
Scrubber	19,504,958	27,334,137	224,268,000	10,251,220	2.7557	2,848,311
<u>Medium Sulfur Illinois No. 6 Coal (Case 2)</u>						
Cold-side ESP	5,289,612	5,382,821	27,041,000	2,061,167	0.5541	202,048
Hot-side ESP	8,725,309	9,810,970	53,519,000	3,607,477	0.9698	536,183
Reverse flow baghouse	15,085,623	17,131,695	134,721,000	7,620,659	2.0486	1,544,013
Collapse + shake bag- house	14,184,497	15,961,988	118,408,000	6,749,633	1.8144	1,101,698
Scrubber	19,653,669	25,246,368	245,204,000	10,703,545	2.8773	3,715,188
<u>High Sulfur Pennsylvania Coal (Case 3)</u>						
Cold-side ESP	7,268,919	8,108,135	35,649,000	2,798,796	0.7524	261,617
Hot-side ESP	11,252,677	12,695,721	65,872,000	4,587,859	1.2333	644,957
Reverse flow baghouse	15,808,259	19,473,208	139,772,000	8,065,957	2.1683	1,616,646
Collapse + shake baghouse	14,877,822	18,266,841	123,377,000	7,175,971	1.9290	1,163,349
Scrubber	21,167,265	34,944,548	333,900,000	14,284,449	3.8399	5,965,479

<sup>a</sup>Installed cost includes equipment and installation costs of the control device and associated ash handling equipment, liquor pumps, etc., and the land cost.

<sup>b</sup>Total annualized cost equals the total of all the power costs associated with the operation of the control device: operating labor, heat loss/cost of reheat, materials cost (lime and makeup water for scrubber), maintenance cost, and all the financial charges including depreciation, taxes, etc. For baghouses, maintenance excludes bag replacement since it does not occur every year, but it is considered in the aggregate cost of ownership and operation (Column 3).

<sup>c</sup>Same as b, expressed in mills/kWh, assuming 500-MWe total capacity and 7,440 operating hours per year.

<sup>d</sup>Same as b but excludes financial charges.

<sup>e</sup>Same as d, expressed in mills/kWh, assuming 500-MWe total capacity and 7,440 operating hours per year.

Control Device	Electrical Power (MWe)	Heat Energy Usage (MWe)	Total Annual Energy Cost (1978 dollars) <sup>c</sup>	a P1
<u>Low Sulfur Montana Rosebud Coal (Case 1)</u>				
Cold-side ESP	0.4121	0.0000	59,486	
Hot-side ESP	1.3374	1.1568 <sup>a</sup>	325,628	
Reverse flow baghouse	1.6183	0.0000	233,581	
Collapse + shake baghouse	1.2698	0.0000	183,285	
Scrubber	8.6721	13.2957 <sup>b</sup>	2,161,362	
<u>Medium Sulfur Illinois No. 6 Coal (Case 2)</u>				
Cold-side ESP	0.4604	0.0000	157,557	
Hot-side ESP	1.0075	1.0704 <sup>a</sup>	467,501	
Reverse flow baghouse	1.4844	0.0000	508,011	
Collapse + shake baghouse	1.1619	0.0000	397,665	
Scrubber	6.1950	12.3022 <sup>b</sup>	2,961,870	
<u>Sulfur Pennsylvania Coal (Case 3)</u>				
Cold-side ESP	0.5980	0.0000	205,116	
Hot-side ESP	1.2690	1.0997 <sup>a</sup>	561,267	
Reverse flow baghouse	1.6692	0.0000	572,523	
Collapse + shake baghouse	1.3380	0.0000	458,911	
Scrubber	15.2598	12.6388 <sup>b</sup>	6,098,600	

<sup>a</sup>In converting the heat loss across hot ESP to an electrical power equivalent, a conversion efficiency of 38.8% (same as the default value for the plant overall thermal efficiency) is assumed.

<sup>b</sup>In converting the stack gas reheat requirement for a scrubber to an electrical power equivalent, it is assumed that steam is used for reheat and the efficiency of a steam-electric turbine is 38.8%.

<sup>c</sup>In computing the total energy cost, the local power cost is used for the electrical portion and for the heat energy portion an energy cost of \$1.75/10<sup>6</sup> Btu is assumed.

in numerous mathematical equations, but they are easily solvable with a hand calculator. A computer program has also been prepared as part of the work done for DOE on this project. The program is an aggregate of the individual models and thus provides for easy application of the models to any given situation.

As illustrated in the case study analysis, use of the model provides a means of comparing control device options based on any or of the following cost criteria:

- . Installed cost,
- . Total annualized cost, \$/year or mills/kwh,
- . Operating cost, \$/year or mills/kwh, and
- . Aggregate cost of ownership and operation over lifetime.

Further, control device comparisons can be made based on energy consumption expressed as:

- . Electrical power required, MWe,
- . Electrical power equivalent of heat,
- . Total power as a percentage of plant capacity, and
- . Annual cost of energy.

The above comparison of energy and economic impacts of various control options provides a valuable means for selecting the optimum method of control for any given system specifications, including power plant site coal characteristics, and emission limits.

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## 1. INTRODUCTION

An important characteristic of most Western coals is that they contain significantly less sulfur than the 2 to 3 pct sulfur content typical of coals in the Interior and Eastern coal regions. The sulfur content of Western coals averages about 0.7 pct, and an average sulfur dioxide removal efficiency of only 30 to 40 pct is required to meet the Federal standard of 1.2 lb SO<sub>2</sub>/MM Btu. At the present time, lime or limestone wet scrubbers are the most commonly used methods for power plant sulfur dioxide emission control. Industrial acceptance of this technology has been slow due to large capital investment requirements, poor operation reliability, and problems associated with sludge disposal. The majority of the lime and limestone systems are located on utility boilers burning high-sulfur Interior and Eastern Province coals. In the West, however, where coal deposits contain significantly less sulfur, several innovative flue gas desulfurization (FGD) techniques are being developed.

One innovative FGD technique developed by the Grand Forks Energy Technology Center (GFETC) is the utilization of alkali in Western coal fly ash in a wet scrubber in lieu of lime or limestone. Studies at GFETC (1) have shown that sufficient amounts of alkali metals, such as calcium, can be leached from fly ash to provide a means of controlling sulfur dioxide emissions from utility boilers burning Western coals. At present there are nearly 2600 MW of generating capacity controlling sulfur dioxide emissions using fly ash alkali. Additionally, approximately 4200 MW of generating capacity are currently under construction or being designed which will utilize the fly ash alkali (FAA) system. These figures include only scrubbers designed for sulfur dioxide control, and not those scrubber systems designed for particulate control on Western boilers, and in which some sulfur dioxide removal occurs. The utilization of Western fly ash alkali has had a significant impact on FGD technology.

A more recent trend in the West has been the use of spray dryers for sulfur dioxide control. This FGD process is based on injecting a concentrated slurry of alkali into the flue gas and atomizing the slurry to promote mass transfer of the sulfur dioxide into the absorbent droplets. The flue gas is maintained above dew point temperatures, thus eliminating reheating requirements. The alkali reagent ends up as a fine particulate and is collected, along with the fly ash particulate, by a fabric filter or an electrostatic precipitator (ESP). The spray dryer FGD concept appears to be suitable for power plants burning Western coals, and at least one Western utility with a new 450-MW plant will employ this concept for sulfur dioxide control.

however, it would be more attractive if water is required. Additionally, dry methods of FGD would be attractive for utilities requiring a retrofit installation. This type of dry process has been under investigation at GFETC since 1975. The materials investigated to date are nahcolite and trona. The application of these materials involves direct injection into the flue gas duct, followed by collection of the sulfur capture agent, along with coal fly ash, using a baghouse or electrostatic precipitator. Thus, there would be no complex chemical equipment to operate, nor flue gas reheat or water requirements, and capital equipment expenditures would be minimal.

The present paper presents a summary of past and present results obtained on a 5000-acfm (saturated) and a 130-scfm pilot plant wet scrubber. Laboratory kinetic studies on dry adsorption of sulfur dioxide using nahcolite and trona, and pilot plant results on dry adsorption of sulfur dioxide by duct injection of nahcolite and trona followed by baghouse and ESP collection.

## 2. ASH ALKALI FGD

An important characteristic of most Western coal ashes is their high alkali content. In general, the alkali content tends to be highest in lignites, and progressively less prevalent in the subbituminous and bituminous coals. As with Western coal ash content, the ash alkali content can vary widely, ranging from under 10 pct to over 50 pct, with significant variations from mine to mine, and even between locations within a single mine. Studies on the utilization of Western coal fly ash alkali in a wet scrubber were pioneered at GFETC using a 130-scfm pilot plant scrubber and, more recently, on a 5000-acfm pilot plant scrubber operating on a side-stream of flue gas from a 238-MW cyclone-fired boiler.

### Laboratory Studies

Laboratory studies at GFETC have shown that the fly ash alkali can be solubilized into an aqueous media, and that solubilization is primarily a function of pH. Figure 1 illustrates the calcium oxide availability as a function of pH for three North Dakota lignite fly ashes. The data were generated using batch leach procedures (1) and, in general, indicate an increase in the amount of calcium oxide as the solution pH decreases. Similar trends are evident for most Western coal fly ashes. There are, however, differences in fly ash leach characteristics from different mines and power plants. The calcium oxide content of the three fly ashes shown in figure 1 are nearly identical; however, the percentage of available calcium at pH 7 varies from about 10 pct to about 40 pct. As the solution pH decreases, however, the differences in solubilities become less significant and tend to approach similar values. The variations in alkali solubility can be attributed to differences in chemical composition of the original coal, and also to differences in the boilers from which the fly ash was derived. The alkali solubility data do indicate that significant amounts of calcium alkali can be leached from the fly ash for use in a wet scrubber.



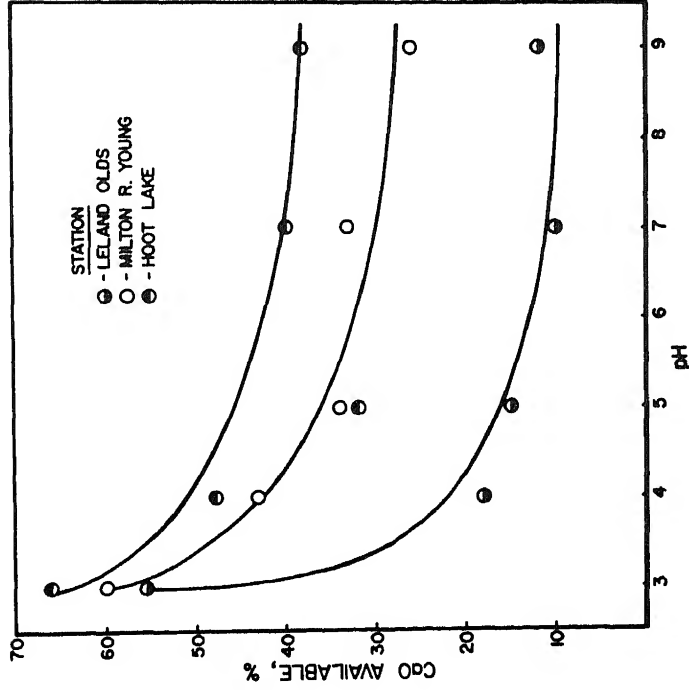


Figure 1. - Effect of pH on calcium oxide availability for three Western lignite fly ashes.

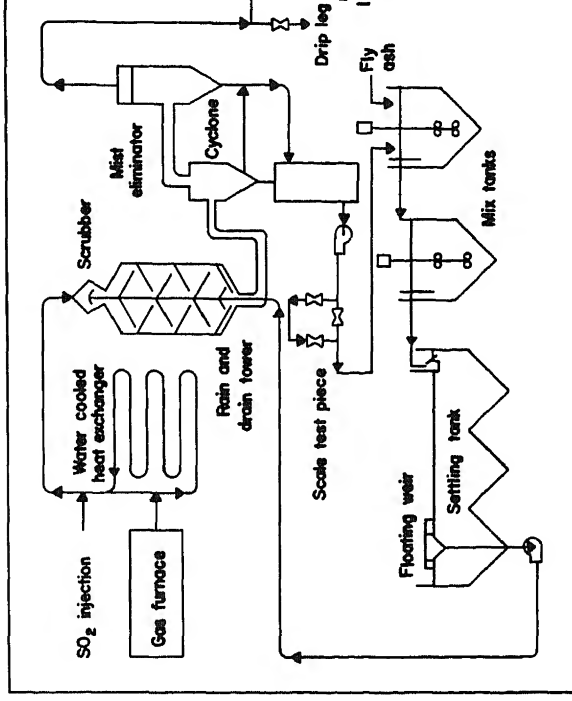


Figure 2. - Flow diagram of 130-scfm pilot scrubber, Grand Forks Energy Technology Center.

the coal ash content, method of firing (pc versus cyclone), and scrubber operating conditions (liquor pH values); however, there is often ample ash alkali available to react with sulfur dioxide in a wet scrubber.

### Pilot Plant Studies

Tests at GFETC have been conducted using a 130-scfm pilot plant scrubber, shown in figure 2, and a 5000-acfm pilot plant scrubber at Center North Dakota, shown in figure 3. Objectives of tests using the 130-scfm pilot scrubber have been to determine sulfur dioxide removal efficiency, calcium sulfate saturation levels and scaling rates as a function of sulfur gas sulfur dioxide concentrations, fly ash add rate and alkali content, supplementary alkali requirements, levels of recirculated suspended solids, liquid-to-gas ratios, amount of makeup water, and total dissolved solids (2,3,4).

The 5000-acfm pilot scrubber was used to conduct a test program under a cooperative agreement among Combustion Equipment Associates (CEA), A. D. Little Company (ADL), Minnkota Power Cooperative (MPC), Square Butte Electric Cooperative (SBEC), Minnesota Power and Light Company (MP&L), GFETC. The four major objectives of the cooperative program were: 1) generate design criteria and determine operating conditions for a 450-scfm scrubber using only fly ash alkali; 2) To conduct a parametric study at operating conditions representative of steady state using fly ash in amounts typically available from both cyclone- and pc-fired boilers; 3) To investigate low pH scrubbing to increase utilization of the fly ash alkali; 4) To investigate the effects of high sodium and magnesium concentrations on fly ash alkali utilization and sulfur dioxide removal efficiencies at low liquid-to-gas ratios (5,6,7,8).

The current test program on the 130-scfm pilot scrubber duplicates the parameters investigated on the 5000-acfm pilot scrubber. The objectives of the tests were to characterize sulfur dioxide removal efficiency, calcium sulfate utilization, rate of scale formation, calcium sulfate saturation level, slurry retention time, and level of recirculated suspended solids on the 130-scfm pilot scrubber. This paper will compare selected results obtained on the 130-scfm pilot plant to results obtained on the 5000-acfm pilot plant.

Figure 4 illustrates the sulfur dioxide removal efficiency and calcium oxide utilization as a function of stoichiometric ratio. The inlet sulfur dioxide and liquid-to-gas (L/G) ratio were maintained at nominal values of 1000 ppm (dry) and 60, respectively. The level of suspended solids varied from about 0.5 pct to about 12 pct. The averaged data obtained on the 5000-acfm pilot scrubber (6) are represented by the solid curve for sulfur dioxide removal, and the dashed line for calcium oxide utilization. The squares represent sulfur dioxide removal efficiency, and the circles represent the corresponding calcium oxide utilization obtained on the 130-scfm pilot scrubber.

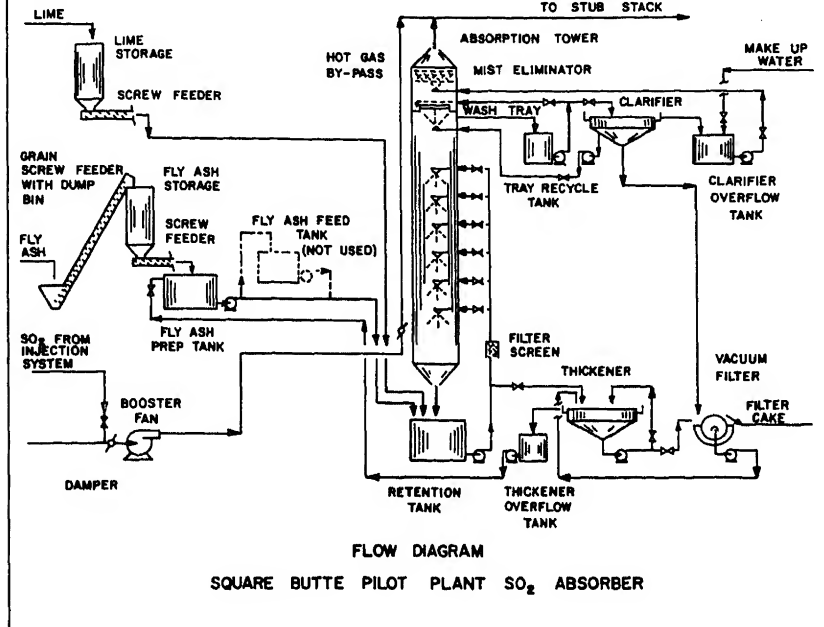


Figure 3. - Flow diagram of the 5000-acfm (saturated) pilot plant scrubber, Square Butte Electric Cooperative, Center, N. Dak.

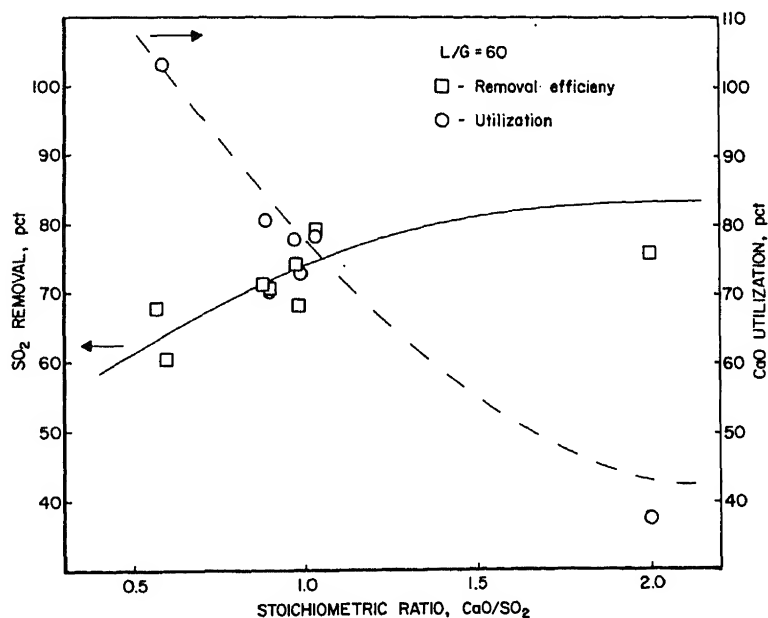


Figure 4. - Sulfur dioxide removal and fly ash CaO utilization as a function of stoichiometric ratio at 1000 ppm SO<sub>2</sub> and a L/G of 60 gal/1000 acf. Data obtained from the 5000-acfm pilot plant scrubber are denoted by the dashed and solid lines. Data obtained from the 120-acfm pilot plant scrubber are denoted by the squares and circles.

Eventually, data from the pilot plant conditions will be obtained, and will provide a means of projecting pilot plant results to a full-scale scrubber using any reagent.

The degree of calcium sulfate saturation is related to scaling potential in a Western scrubber. Control of scaling must be approached differently for low-sulfur Western coals than for Eastern coals, primarily due to the high state of sulfur oxidation. Control of scale formation in the fly ash alkali system will depend most directly on maintaining a relatively constant pH, and on circulating a sufficiently high level of suspended solids, allowing sufficient time and mixing to desaturate calcium sulfate in solution. The recirculated suspended solids are composed of calcium sulfate and undissolved fly ash particles, which can assist in maintaining the pH at a constant value. If the sulfur dioxide levels should significantly increase, the undissolved fly ash suspended solids react with the excess sulfur dioxide and effectively dampen large pH fluctuations.

The effects of suspended solids and retention time on calcium sulfate saturation on the 130-scfm pilot plant scrubber are not clearly defined. Test data using suspended solids ranging from 0.5 pct up to 11.5 pct indicate no effect on saturation, remaining approximately constant at about 200 pct. These results do not agree with results obtained on the 5000-acfm scrubber, which indicate a decrease in saturation values in the suspended solids range of 1 to 6 pct, and no effect from 6 pct up to about 12 pct. The saturation values were calculated using activity coefficients. Data generated for liquor retention times from 4 minutes to 16 minutes also indicate no effect on calcium sulfate saturation, and the values were generally constant at about 200 pct. However, scale formation was not detected during experiments on either the 130-scfm pilot plant scrubber or on the 5000-acfm pilot plant scrubber.

One characteristic of scrubbing with fly ash alkali is the high level of dissolved solids, specifically magnesium, sodium, and sulfate. The sulfate levels, which represent 99 pct of the soluble sulfur forms in the scrubber liquors from the 130-scfm and 5000-acfm pilot plant scrubbers, may range up to 8 pct and contribute directly to the high saturation values. The magnesium and sodium levels are also high, reaching concentration levels up to 10 pct. The overall effect of the high sulfate levels is to increase the calcium sulfate saturation values, with the magnesium and sodium levels decreasing the saturation values.

A summary of physical characteristics of sludge (8) generated during a two-week material balance test on the 5000-acfm pilot plant scrubber is shown in Table 1.

Porosity.....	0.64 to 0.77
Moisture.....pct..	23 to 38
Unconfined compressive strength.....kg/cm <sup>2</sup> ..	1.0 to 2.5

1/ Range of values for ten samples.

Since the predominant sulfur form in the scrubber liquor is sulfate, sludge material is enriched in calcium sulfate in addition to unreacted fly ash. Therefore, the resulting sludge has excellent settling characteristics and is readily dewatered. Pozzolan activity due to unreacted fly ash can be visually observed, and is also demonstrated by the relatively large values of unconfined compressive strength shown in Table 1. The permeability coefficient for the sludge material ranged from  $2 \times 10^{-6}$  cm/sec to 6.5 x 10<sup>-6</sup> cm/sec. These values are one to two orders of magnitude less than lime/sludge materials and should pose less of a threat to the environment when disposed in a landfill.

### 3. DRY ADSORPTION OF SULFUR DIOXIDE

Many utilities in the West are located in areas where water supplies are scarce. A true "dry" sulfur dioxide removal system would be an attractive alternative to a wet scrubber system. Additional advantages of a dry FGD system are: 1) no complex chemical plant to operate; 2) high reliability; 3) immediate response to fluctuation in sulfur dioxide levels; 4) disposal of a dry waste material; 5) less capital investment requirements; 6) lower operating expenses; and 7) more readily adaptable to retrofit situations. The FGD technology may be more suitable for utilities burning Western coals since the low sulfur content would require smaller quantities of sorbent material to meet the existing NSPS of 1.2 lb SO<sub>2</sub>/MM Btu, or the proposed standard of 85 pct removal.

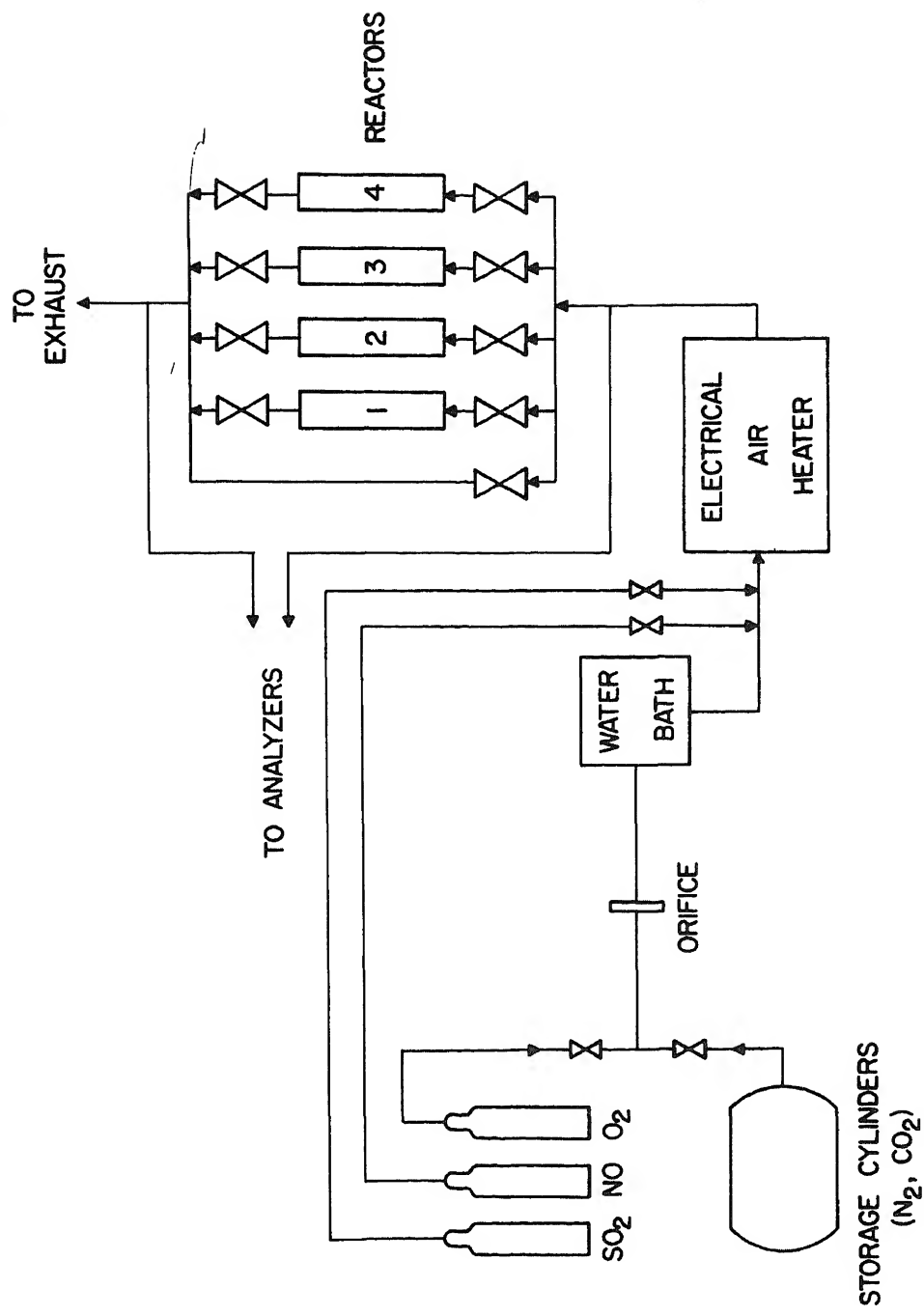
The objectives of the GFETC dry adsorption program are to determine the suitability of various materials as dry adsorbents, and to conduct larger scale parametric tests on promising adsorbents. Two promising materials are nahcolite and trona, which are naturally-occurring mixtures of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) and sodium bicarbonate (NaHCO<sub>3</sub>). This report presents selected results on kinetic studies using laboratory batch-type fixed-bed reactors, and on pilot plant tests using a 75-lb/hr pulverized coal-fired furnace with either a baghouse or an ESP for particulate control.

figure 5. Simulated flue gas of the desired composition was passed through the reactor containing a thin bed of adsorbent.

When nahcolite and trona are exposed to elevated temperatures, sodium bicarbonate is converted to sodium carbonate, resulting in a significant change in the specific surface area. The bicarbonate-to-carbonate conversion product is commonly said to be activated. Figures 6 and 7 illustrate the effects of temperature and time on surface area for nahcolite and trona, respectively. For both adsorbents, the maximum specific surface area was achieved at about 600° F. At temperatures above 600° F, the specific surface area decreased significantly due to sintering of the particle surface. The sintering effect was verified by SEM photographs (10). The data indicate that the bicarbonate-to-carbonate conversion occurs more rapidly for nahcolite (see fig. 6) than for trona (see fig. 7), especially at temperatures above 500° F. Additionally, nahcolite has a higher specific surface area than trona over all temperature ranges. In the present experiments, both adsorbents were preheated at 600° F for two hours to ensure an equivalent starting material for all test conditions. Future plans include redesigning the reactor to allow charging the adsorbents directly into the preheated batch reactor with gas flow established.

Figure 8 illustrates the effect of temperature on sulfur dioxide adsorption using nahcolite. In general, the sulfur dioxide adsorption profiles indicate an initial rapid increase which levels off to a relatively constant value for the time range investigated. For the time range of zero to 200 seconds, the adsorption rate increases with temperature up to about 650° F. However, the data collected at 750° F indicate a slight reduction in adsorption. The decreased adsorption at 750° F may be attributed to sintering of the particle surface, causing a decrease in specific surface area.

Figure 9 illustrates the effect of particle size on sulfur dioxide adsorbence using nahcolite. The results indicate that as the particle size decreases from an average particle diameter ( $\bar{D}_p$ ) of 0.5 mm to 0.09 mm, the amount of sulfur dioxide adsorbed was doubled. The adsorbent utilization for the 0.09 mm particles was about 98 pct after 200 seconds. An examination of the reacted nahcolite using SEM techniques indicated that the lower adsorption of the larger particles was due to pore blockage by an ash layer of sodium sulfate. For both the 0.5 mm and 0.19 mm reacted particles, the investigation indicates a sodium sulfate ash layer penetration of about 0.1 mm. These results indicate that an optimum particle size exists, below which additional adsorbent size reduction is not beneficial. The optimum adsorbent size would depend on the specific application, gas-solid contact temperature, and residence times.



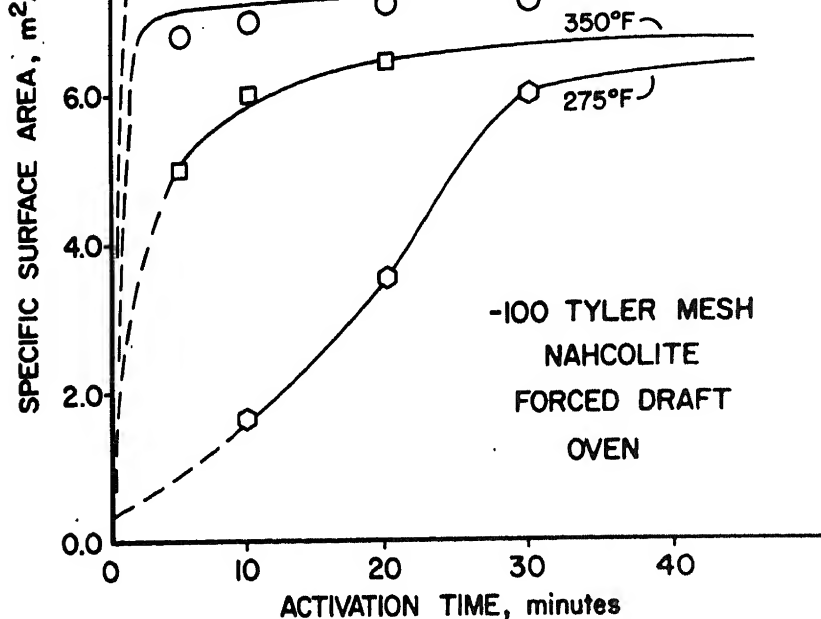


Figure 6. - Effect of temperature and time on specific surface area for nahcolite.

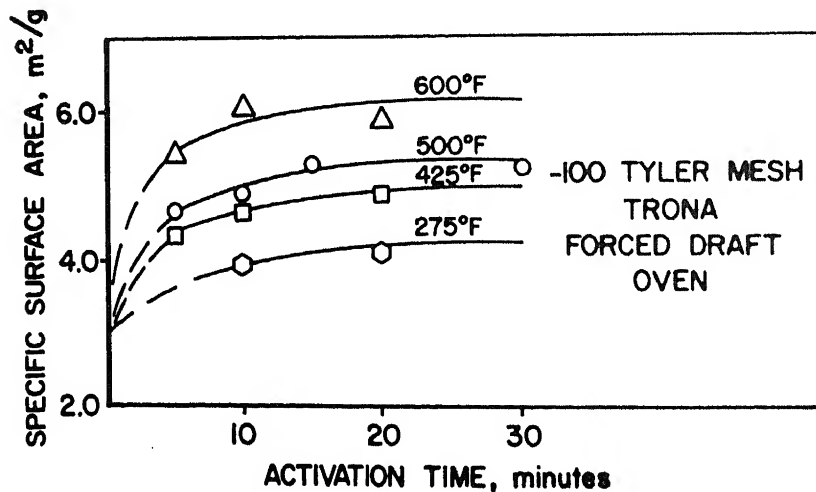


Figure 7. - Effect of temperature and time on specific surface area for trona.



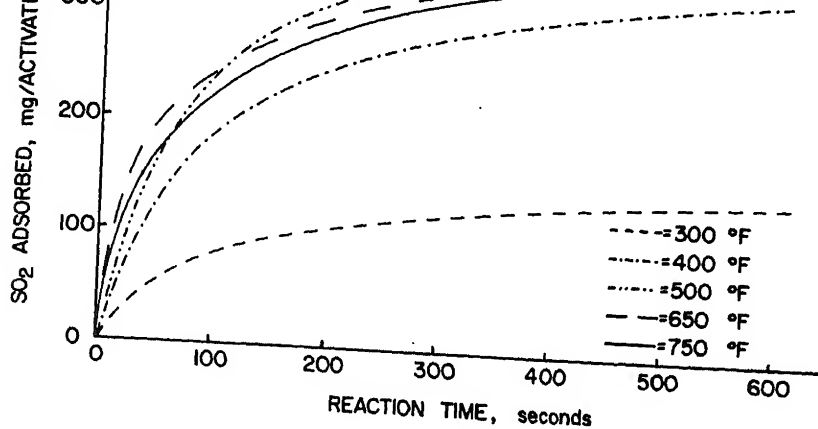


Figure 8. - Temperature effect on nahcolite sulfur dioxide adsorbance.

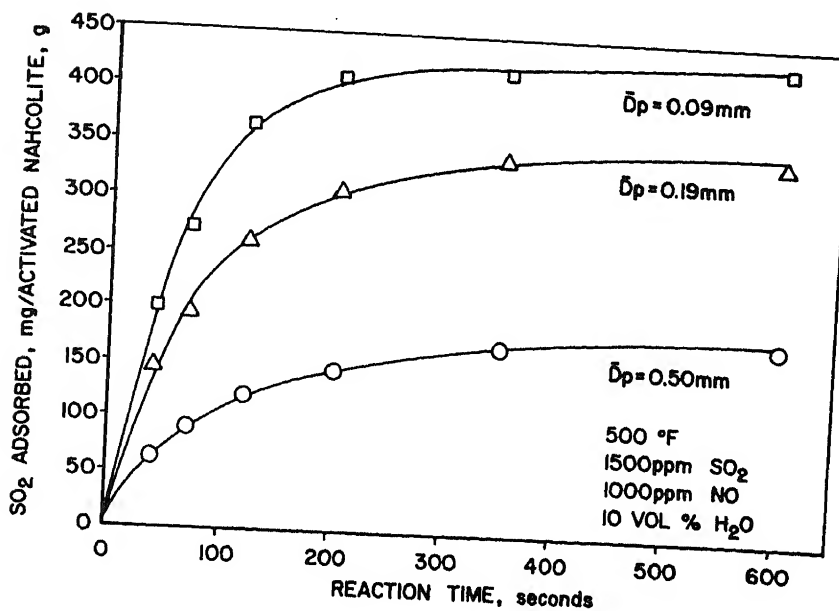


Figure 9. - Effect of nahcolite particle size on sulfur dioxide adsorbance.

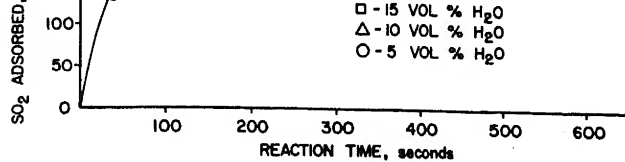
Figure 12 illustrates the sulfur dioxide adsorbence using both trona and nahcolite at identical experimental conditions. The data indicate adsorbence for trona compared to nahcolite at each condition investigated. Their results may be attributed to the lower specific surface area (see fig. 7). However, the differences may be less significant in applications where lower temperatures or longer retention times are required, or smaller trona particles are utilized.

Analyses of reacted nahcolite and trona obtained from the above tests for nitrites and nitrates indicate little nitric oxide adsorption. When tests with nahcolite were repeated without sulfur dioxide in the gas, appreciable amounts of nitric oxide were adsorbed, as shown in Figure 13. The dashed line represents nitric oxide adsorption in the absence of sulfur dioxide. The solid line represents nitric oxide adsorption in the presence of 1500 ppm sulfur dioxide. The data indicate significant nitric oxide adsorption in the absence of sulfur dioxide, and the adsorbent utilization approaches 97 pct for a reaction time of 5400 seconds (90 minutes). The results indicate a competitive reaction between sulfur dioxide and nitric oxide for the active sites of the nahcolite adsorbent, with the sulfur dioxide dominating the reaction kinetics. Preliminary data indicate that greater amounts of nitric oxides are adsorbed at 300° F than at higher temperatures. This apparent decrease in adsorption may be due to the thermal instability of the reaction product; however, additional studies are required. Both nitric oxide and nitrogen dioxide adsorption will be investigated in greater detail in future work.

### Pilot Plant Studies

Tests have been performed utilizing the GFETC 75-lb/hr, pc-fired pilot ESP facility, shown schematically in figure 14. The subbituminous coal burned in this study was provided by Utah Power and Light (UP&L) from the Kemmerer Mine at Kemmerer, Wyoming. UP&L also provided the nahcolite, obtaining them from the Superior Oil Company.

The pilot plant program was designed to study dry sulfur dioxide removal as a function of adsorbent material, injection temperature, retention time, stoichiometric ratio, adsorbent particle size, and collection efficiency under simulated power plant conditions. Flue gas sulfur dioxide removal could occur in any one of three regions in the system: 1) during sorbent suspension in the flue gas, 2) during collection in an electrostatic precipitator, and 3) during collection in the filter (baghouse). The sulfur dioxide concentrations were maintained in the range of 850 to 1000 ppm, approximating the combustion of Kemmerer coal at a one pct as-received sulfur content. The present results represent the primary work completed to date.



dioxide adsorbance

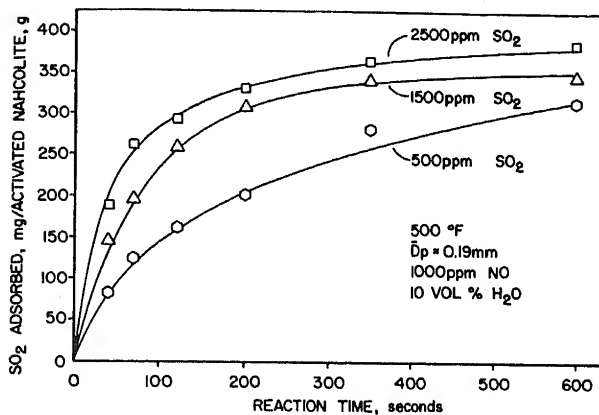


Figure 11. - Nahcolite adsorption of various sulfur dioxide concentrations.

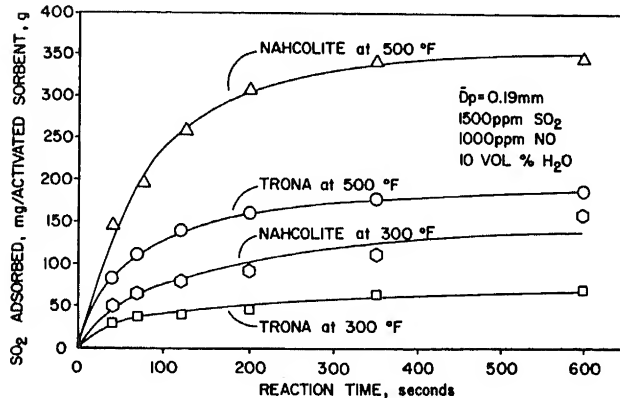


Figure 12. - Comparison of nahcolite and trona sulfur dioxide adsorption at two temperatures.

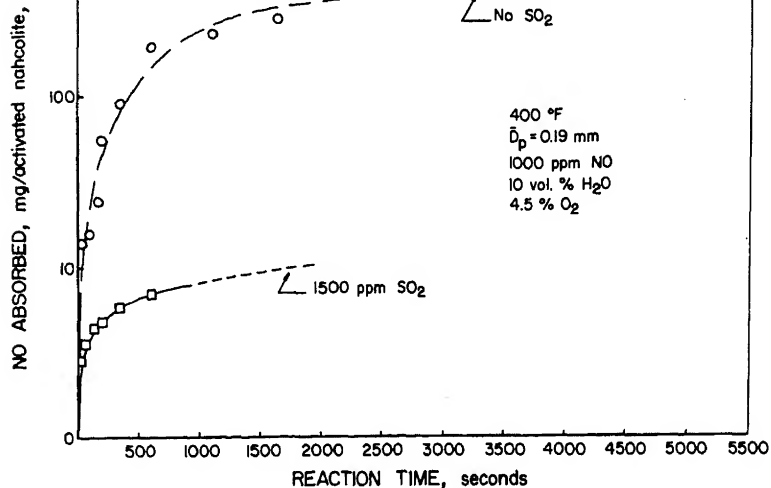


Figure 13. - Nitric oxide adsorbance using nahcolite with and without sulfur dioxide.

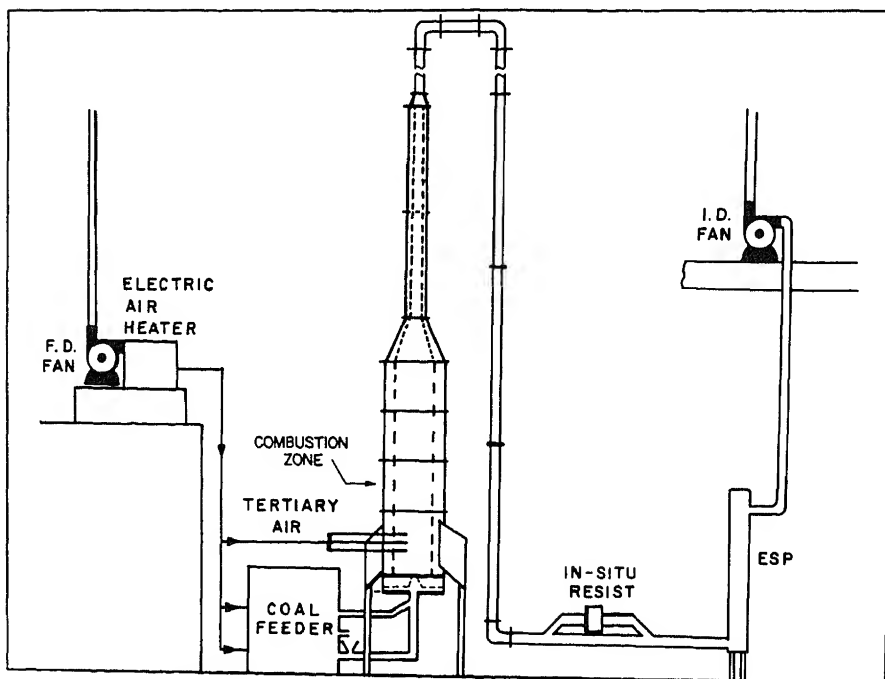


Figure 14. - Schematic of 75-lb/hr pc-fired pilot plant combustor at GFETC.

into the furnace burner were performed in two ways. In the first case, the makeup sulfur dioxide (required to increase the normal sulfur dioxide level of approximately 320 ppm to the desired level of 925 ppm) was injected after the combustion gases had been cooled to below 2000° F. In the second case, the makeup sulfur dioxide was injected along with the coal into the burner. Data from these tests are summarized in Table 2. In the first case at stoichiometric ratios of 0.9 to 1.8, sulfur dioxide removals ranged from 21 to 39 pct and overall utilizations were nearly constant at 22 pct. These results would indicate an optimum utilization of about 22 pct regardless of adsorbent material or stoichiometric ratio. From 62 to 100 pct of the overall sulfur dioxide removal occurred in zone A (flue gas above 1400° F). The 39 pct maximum removal observed under case 1 conditions is approximately equivalent to that fraction of the total sulfur dioxide resulting from combustion of the coal (320 ppm out of 925 ppm).

Results obtained under case 2 conditions indicate a range of sulfur dioxide removals from 32 to 99 pct at stoichiometric ratios of 0.8 to 2.6. Virtually all of the removal occurred in zone A. Utilizations averaged 41 pct with, again, very little variation with stoichiometric ratio or adsorbent material. These results indicate that nearly all of the sulfur dioxide removal occurs at temperatures above 2000° F when the adsorbents are injected into the flame region. The events occurring in such a process most likely correspond to those postulated for the action of sodium in promoting ash fouling of heat exchange tubes in coal-fired boilers (11). The sodium material volatilizes in the coal flame, forming a reactive vapor which combines rapidly with gaseous sulfur dioxide or sulfur trioxide to form a fine sodium sulfate particulate when cooled. Burner injection of sodium materials for sulfur dioxide control could not be recommended due to the near certainty that severe ash fouling would result in the boiler superheat and reheat sections. To evaluate the potential ash fouling problem, an experiment using nahcolite injected into the burner was conducted using the 75-lb/hr, pc-fired ash fouling furnace at GFETC. The result was formation of a molten, glassy, flowing slag on the simulated secondary superheat tubes. This most assuredly would be an impossible condition in a full-scale boiler.

### Adsorption in Flue Gas Suspension

Tests to evaluate the sulfur dioxide adsorbence of nahcolite and trona in a flue gas stream, with injection temperatures ranging from 360 to 1515° F, indicate an optimum injection temperature of about 650° F for both materials. The existence of an optimum injection temperature is in agreement with the results obtained in the laboratory kinetic study (see figures 6, 7, and 8). The data obtained at 650° F are presented in Table 3.

TABLE 2. - Sulfur dioxide adsorption results with adsorbent injected into the flame

Adsorbent material	Stoichiometric Ratio	Zone A			Zone B			Zone C		
		Flue Gas Prior to 1400° F		Utilization, pct	Zone A + Flue Gas Prior to ESP		Utilization, pct	Zone A + B + ESP		Utilization, pct
		Residence time, sec.	Removal, pct		Residence time, sec.	Removal, pct		Residence time, sec.	Removal, pct	
SE 1:1/										
ncolite	0.92	3.1	17.7	19.3	4.0	19.9	21.7	5.0	21.6	23.
ncolite	1.00	3.0	13.2	13.2	3.9	16.5	16.5	4.9	21.3	21.
ncolite	1.83	2.9	39.1	21.4	3.7	39.1	21.4	4.6	39.1	21.
na	1.18	2.9	22.1	18.6	3.7	24.6	20.7	4.7	26.5	22.
E 2:2/										
ncolite	0.79	3.1	31.6	42.6	5.0	31.6	42.6	6.0	31.6	42.
ncolite	2.04	3.1	89.4	43.3	4.9	89.4	43.3	6.0	89.4	43.
na	1.34	3.1	53.4	39.9	5.0	53.4	39.9	6.1	53.4	39.
na	2.60	3.0	97.5	37.4	4.8	98.3	37.8	5.8	98.8	37.

adsorbent into burner along with coal, makeup sulfur dioxide injected downstream (flue gas below 2000° F).

adsorbent and makeup sulfur dioxide injected into burner along with coal.

Nahcolite	100	640	3.1	0.71	24.0	33.9
	100	640	3.1	1.52	48.2	31.8
Nahcolite	200	650	3.5	1.47	45.6	31.0
	200	650	3.2	1.84	61.2	33.3
Trona	100	640	3.1	1.96	33.0	16.7
	100	630	1.2	1.03	25.6	24.8

The data indicate that, although a sulfur dioxide removal greater than 60 pct was achieved in the best case, the low adsorbent utilization values would probably make such a scheme unattractive for economic reasons. As the selected data illustrate, there is not a clearcut difference for in-duct sulfur dioxide removal between the minus 100 and minus 200 mesh nahcolite. As in flame injection, utilization of nahcolite adsorbent was independent of stoichiometric ratio at the conditions studied. There is some indication from the whole body of data obtained that below the residence times available in a power plant, greater than three seconds, and at injection temperatures below the optimum 650° F, the finer material performs somewhat better. At injection temperatures above about 800° F, there is no apparent difference between minus 100 mesh nahcolite and minus 100 mesh trona. At injection temperatures near the optimum and below, the minus 100 mesh nahcolite has a distinct advantage. Although tests have not been run to evaluate a finer trona for duct sulfur dioxide adsorption, the data comparing the two size ranges of nahcolite would lead one to expect somewhat improved performance for a minus 200 mesh trona.

#### Adsorption in a Pilot Plant ESP

A series of tests were conducted to study the nahcolite and trona adsorbents in systems which include an ESP. The motivation was twofold: 1) to evaluate such a system for sulfur dioxide removal, and 2) to determine the effect of the injection of relatively large quantities of sodium material on ESP operation. During ESP operation, the overall sulfur dioxide removals and adsorbent utilizations were increased an average of 55 pct above that occurring in suspension. It is felt that this apparent improvement due to the presence of the ESP might not be as substantial in a full-scale precipitator. At least two factors would tend to reduce the potential effectiveness of the increased flue gas residence time in a full-scale precipitator. In the first place, the majority of the removal of the input particulate mass in a full-scale ESP occurs in the first few feet, significantly reducing the portion of the apparent long residence time which is effectively adsorbent/flue gas contact time. Secondly, the collection electrode of the pilot ESP utilized

resistivity, there was virtually no change in ESP mass removal efficiency. The doubling or tripling of the inlet particulate concentration, however, resulted in a twofold increase in the outlet particulate concentrations in all cases studied.

### Adsorption in a Pilot Plant Baghouse

A series of tests were conducted to study the nahcolite and trona adsorbents in systems which include a baghouse. The pilot baghouse was substituted for the pilot ESP in the system illustrated in figure 14. Tests with nahcolite indicate that utilization in the baghouse was independent of adsorbent size below 100 mesh, injection temperature, and stoichiometric ratio at baghouse cycles of 45 to 60 minutes. In these cases, adsorbent injection was maintained at a constant level for the entire cycle. The overall adsorbent utilizations fell in the range from 63 to 77 pct for all cases. More tests are required to evaluate the effect of baghouse operating temperature.

The particle size of the adsorbent appears to be a significant factor when trona is used as the adsorbent, as shown in figure 15. The utilizations shown in figure 15 for the minus 200 mesh trona fall within the range determined for nahcolite (63 to 77 pct), indicating that properly sized trona can be as effective as nahcolite when used in conjunction with a baghouse. More tests are required to establish what additional parameters might significantly effect trona sulfur dioxide adsorption in a baghouse.

Figure 16 illustrates an interesting aspect in the development of dry sulfur dioxide adsorption techniques utilizing a baghouse. In this case, the trona at an overall stoichiometric ratio of 0.96 was injected during the first 8 minutes of a 74-minute test. A series of such curves over a variety of cycle durations and injection schemes should aid in the development of optimum dry adsorbent injection methods and baghouse designs for use in a sulfur dioxide removal system. Optimization of the system should include evaluation of adsorbent injection techniques and baghouse cycling. In general, dry sulfur dioxide adsorption utilizing nahcolite and trona in conjunction with a baghouse appears to have potential as a flue gas desulfurization technique. Continuation of the current test program is certainly warranted. Larger-scale testing to confirm the potential indicated by this work, as well as that of others (12,13) should be planned in the near future.



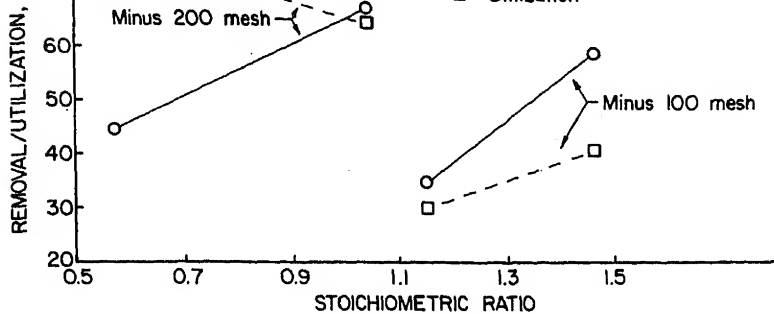


Figure 15. - Adsorbent utilization (denoted by dashed line) and sulfur dioxide removal (denoted by solid line) as a function of stoichiometric ratio using minus 100 and minus 200 mesh trona in a baghouse.

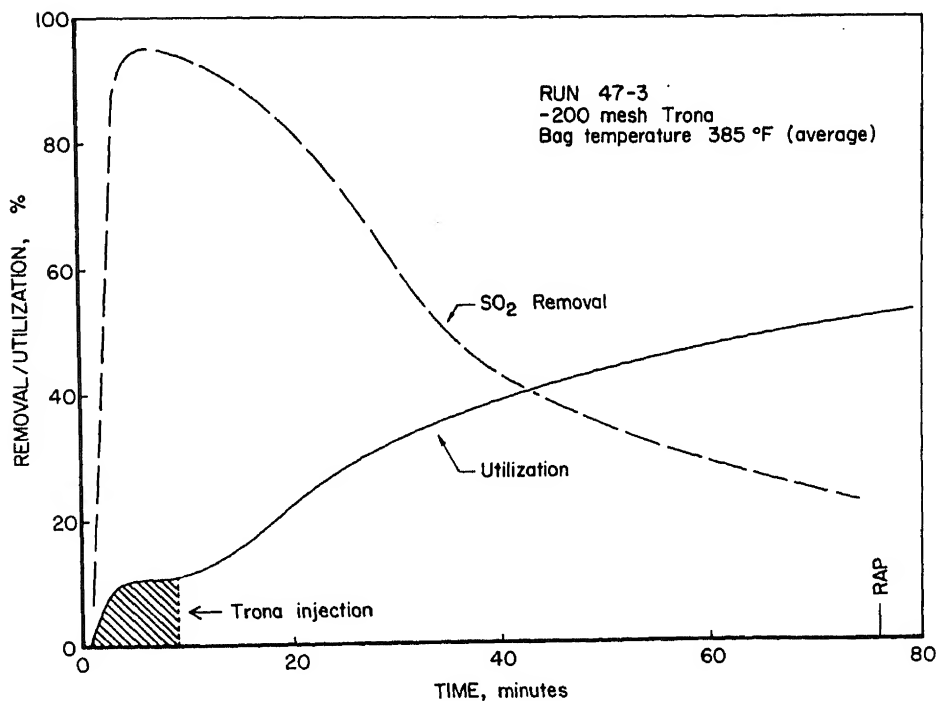


Figure 16. - Sulfur dioxide adsorption results utilizing minus 200 mesh trona with a baghouse and non-continuous adsorbent injection.

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## Introduction

The literature on past and current global CO<sub>2</sub> studies yields a perspective on the bounds of the potential atmospheric CO<sub>2</sub> problem. During the last one hundred years or so, the release of fossil carbon as CO<sub>2</sub> has increased at an exponential rate as shown in Figure 1.<sup>1</sup> As a result, the concentration of CO<sub>2</sub> contained in the atmosphere has grown by about 12%, increasing from about 295 ppm by volume in 1960 (pre-industrial revolution) to the current level of 331 ppm. Except for short periods during World Wars I and II and the depression, the release rate of fossil carbon has increased at the rate of about 4.3% per year.<sup>2</sup> At present, with no CO<sub>2</sub> emission controls, about  $5 \times 10^9$  metric tons of carbon per year as CO<sub>2</sub> are emitted to the atmosphere by the burning of fossil fuels from worldwide sources. About 50% of this carbon can be accounted for by the increase in the CO<sub>2</sub> concentration of the atmosphere. The remaining carbon is assumed to be absorbed by the oceans and by the land biota, in unknown proportions. Deforestation considerations and the possibility of the release of CO<sub>2</sub> from the Pacific Ocean waters south of the equator due to the "Southern Oscillation",<sup>3</sup> a naturally occurring phenomenon of unknown cause, tend to becloud the issue. A better understanding of the carbon cycle is definitely needed.

If the use of fossil fuels continued to grow at 4.3% per year until the estimated supplies thereof were exhausted, the use rate at the end of this period would be almost 64 times the current use rate, and the total CO<sub>2</sub> injected into the atmosphere, during this period, would be about 12 times the pre-industrial content of the atmosphere. Obviously, such a use pattern cannot be tolerated; however, based on more realistic assumptions, it is predicted that the concentration of atmospheric CO<sub>2</sub>, relative to the pre-industrial value, could increase by a factor of from about 2 (low use case) to about 5 (high use case) during the next one hundred years. The low use case corresponds to a fossil fuel growth rate of 2% per year until the year 2025, followed by a symmetrical decrease as alternative and renewable energy sources become more available and the use of fossil fuels is discouraged. The high use case corresponds to an initial annual growth rate of 4.3% with subsequent reductions in proportion to the ultimate fossil fuel supply that has been consumed. In both cases, about 50% of the emitted fossil carbon is assumed to be taken up by the oceans and land biota.

Of primary concern is the warming ("greenhouse") effect which could be produced by these increased CO<sub>2</sub> concentrations due to the absorption by CO<sub>2</sub> of a portion of the infrared radiation returning to space from the earth [the infrared absorption spectrum of CO<sub>2</sub> shows strong absorption bands at

regime (the regular pattern of seasonal rainfall) as well as the earth's albedo (reflection power).<sup>4</sup> The amount of warming produced by a given concentration increase is estimated at 1 to 5°K per doubling of the CO<sub>2</sub> concentration.<sup>2</sup> For the low use case described above, this corresponds to a mean global temperature rise of from about 1 to 5°K over the next one hundred years and from about 2 to 10°K for the high case. A temperature of 1°C during this period may be acceptable, however, a rise of 10°K would probably cause catastrophic effects.

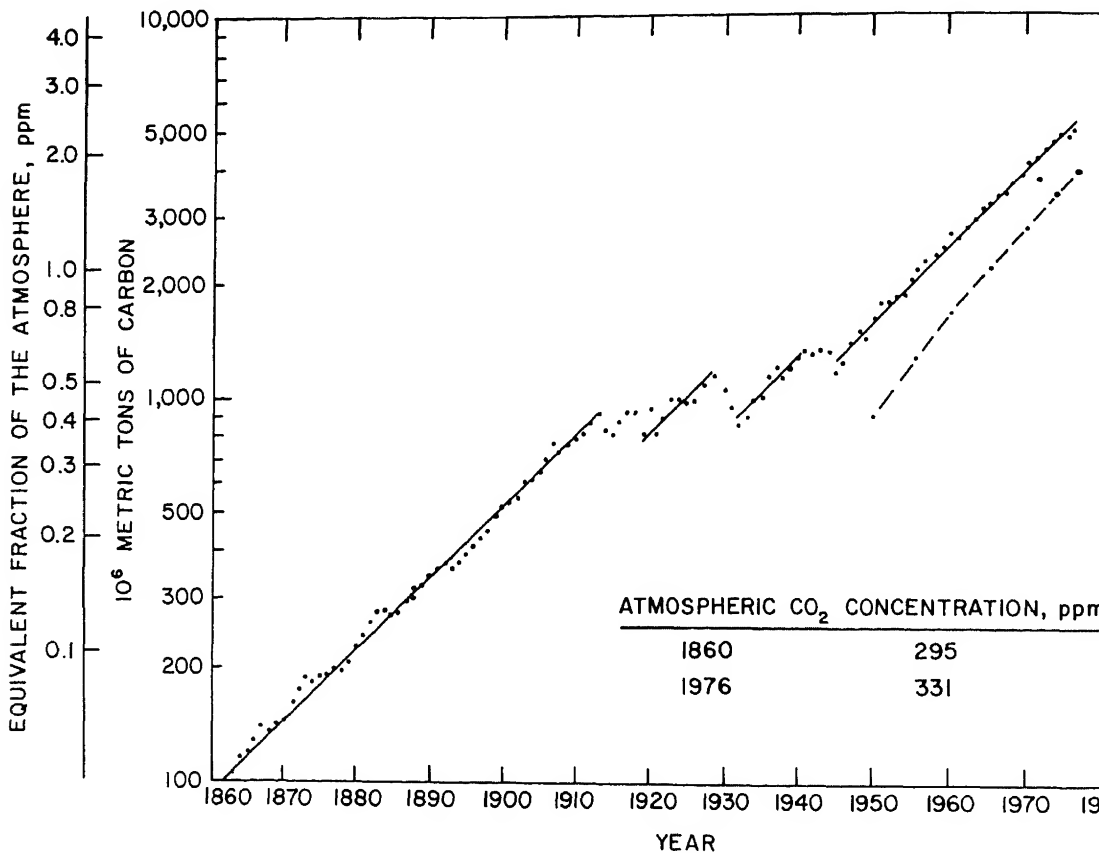


FIGURE 1: CO<sub>2</sub> PRODUCTION FROM FOSSIL FUELS AND CEMENT

— WORLDWIDE  
 --- WORLDWIDE LESS U.S. SOURCES

Increased concentrations of particulate matter (and aerosols) in the global air mass could produce a cooling effect by backscatter of incoming solar radiation and thus counteract, to some degree, the warming produced by increasing CO<sub>2</sub> levels. However, environmental emission regulations on particulates, as well as on other identified pollutants, have become more and more stringent since the mid-1970s.

Since there is a chance that naturally occurring and/or anthropogenic opposing factors will not just counter the effects of increasing CO<sub>2</sub> levels, it may be necessary to limit industrial CO<sub>2</sub> emissions in the future. Up to the present, there has been practically no concern about the health or environmental effects of CO<sub>2</sub> discharge; accordingly, there are no regulations applicable to CO<sub>2</sub> emissions. Options for CO<sub>2</sub> control have received little attention and although preliminary evaluations indicate that control is theoretically possible, it may not be technically or economically practicable. It thus becomes important at this time to examine CO<sub>2</sub> control options to determine the technical feasibilities and the economic costs, should the need arise for CO<sub>2</sub> control.

### Impact of US Emissions

In order to determine the impact of fossil fuel use in the United States on overall (worldwide) CO<sub>2</sub> emissions, we have superimposed several points on Figure 1, based on US fuel use data for the years 1950, 1955, 1960, 1965, 1970, 1973,<sup>5</sup> and 1976.<sup>1</sup> The points were obtained by subtracting the estimated emissions of carbon (as CO<sub>2</sub>) by US sources from the corresponding worldwide emissions for each of the above years, and thus indicate the quantities of carbon that would have been emitted if the US had not burned any fossil fuel during these years. The reduction in carbon (and thus in CO<sub>2</sub>) by this hypothetical non-use of fossil fuels in the US ranges from 0.32 ppm in 1950 to 0.64 ppm in 1973 (and in 1976) as given in Table 1. However, during this period the percentage of the total yearly emissions contributed by the US decreased from 43% in 1950 to 27% in 1976. This is due to an increasing rate of fossil fuel usage in developing nations and a decreasing rate in the US. Furthermore, it is projected that the contributions to global CO<sub>2</sub> production by the US and Canada will decrease to about 8% by the year 2025. Developing nations will account for 36% of the CO<sub>2</sub> production, the USSR and Eastern Europe 27%, Asia 19%, Western Europe 7%, and Japan and Australia 3%.<sup>1</sup> Therefore, it would appear that a worldwide effort would be required to effectively control the level of atmospheric CO<sub>2</sub>. A unilateral effort by any one nation probably would not be very effective.

### Impact of Coal Utilization

Table 2 contains a source distribution of carbon (CO<sub>2</sub>) produced from major worldwide sources during the years 1970 through 1976.<sup>1</sup> For the year 1976, using the heating values of 18,000 BTU/lb of contained carbon for coal, 22,400 BTU/lb carbon for fuel oil and 31,500 BTU/lb carbon for natural gas, and assuming that all fossil energy was produced by the burning of solid coal, the carbon release to the atmosphere would have been roughly  $6 \times 10^9$  metric tons or about 1.2 times the quantity actually emitted. Energy differences required in mining versus drilling, preparation, transportation, etc. and in combustion efficiencies were not taken into account. Note that the weight ratio of CO<sub>2</sub> produced by the burning of coal to that produced by the burning of natural gas, for the same energy output, is about 1.8 and for

atmosphere would have been even greater than  $6 \times 10^6$  metric tons, due to inefficiencies in the gasification and liquefaction processes as will be shown below. Thus, added reliance on coal for energy production could compound the atmospheric release rate of  $\text{CO}_2$ , which has been increasing exponentially since 1860.

Table 1

U.S. CONTRIBUTION TO ATMOSPHERIC  $\text{CO}_2$  EMISSIONS  
COMPARED TO ALL OTHER WORLDWIDE SOURCES<sup>1,5</sup>

Year	Incremental Atmospheric $\text{CO}_2$ Concentration in ppm		% U.S. Contribution	% Others
	Worldwide	U.S.		
1950	0.74	0.32	43	57
1955	0.92	0.36	39	61
1960	1.18	0.39	33	67
1965	1.47	0.46	31	69
1970	2.00	0.58	29	71
1973	2.27	0.64	28	72
1976	2.38	0.64	27	73
2025 Est.			8	92*

\* Developing nations estimated to account for 36% of total worldwide  $\text{CO}_2$  emissions.

Impact of Alternative Energy Sources

The expected reduction in the US contribution to worldwide atmospheric  $\text{CO}_2$  emissions is partially attributed to the development and implementation of alternative energy sources, which includes, nuclear (fission and fusion), geothermal and solar. The impact of these alternatives in the US depends to a great extent on four factors: (1) the demand growth for energy in the US, (2) the availability of the technology, (3) the capital and production costs, and (4) the supply of world petroleum sources and the demand of developing countries for petroleum and coal resources. Although uncertainties

the US in the next 50 to 100 years as listed in Tables 3 and 4. Thus, if the energy demand no more than doubles in the next 50 years, and the fossil fractional use decreases about in half the US would then contribute approximately the same amount as at present to the world atmospheric CO<sub>2</sub> emissions, as indicated by the CO<sub>2</sub> Index in Table 4. However, the other countries would exceed their present contributions as they develop technologically at a higher rate. Eventually even these countries will acquire alternative energy sources and the CO<sub>2</sub> emissions may then become stabilized.

Table 2

WORLD-WIDE CO<sub>2</sub> EMISSIONS BY SOURCE

All entries in 10<sup>6</sup> metric tons carbon as CO<sub>2</sub>

Source	1970	1971	1972	1973	1974	1975	1976	1976 Distribution %
Coal	1497	1479	1499	1527	1550	1626	1676	33.2
Lignite	237	239	243	246	246	249	260	5.1
Crude Petroleum & N.G. Liquids	1803	1907	2011	2203	2213	2107	2224	44.1
Natural Gas	545	583	614	646	659	665	675	13.4
Natural Gas Flared	90	94	100	110	113	105	113	2.2
Cement	82	88	93	95	95	100	99	2.0
Total carbon as CO <sub>2</sub>	4254	4390	4560	4827	4876	4852	5047	
Incremental atm CO <sub>2</sub> Conc. (ppm)	2.00	2.07	2.15	2.27	2.29	2.28	2.38	
U.S. Emissions Contribution	0.58			0.64			0.64	

In the interim, there is thus sufficient incentives, even when considering alternative energy sources, to systematically examine the technological and engineering factors for controlling CO<sub>2</sub> emissions. The systematic study would be of value for identifying candidate CO<sub>2</sub> control scenarios and to determine their technical and economic practicabilities. The environmental control technology of CO<sub>2</sub> may be of short term value for the US but of much more value in the longer term for worldwide purposes.

ANTICIPATED DISTRIBUTION OF ALTERNATE ENERGY SOURCES  
FOR THE U.S. IN THE NEXT 50 TO 100 YEARS

Source	Percent of Demand		
	1975	2025	2075
Fossil (coal, oil and gas)	90%	50%	30%
Nuclear (Fusion and Fission)	5	20	30
Solar	0	20	30
Hydro, Geothermal and others	5	10	10
Total	100	100	100

Table 4

U.S. AND WORLD ENERGY GROWTH AND  
DISTRIBUTION OF ALTERNATIVE SOURCES

Region	1975			2025	
	Quads	Fraction Fossil	CO <sub>2</sub> Index *	Quads	Fraction Fossil
U.S.	75	0.90	67.5	150	0.50
Other Nations	175	1.00	175.0	1100	0.84
World (total)	250	0.97	242.5	1250	0.80

\* CO<sub>2</sub> index is product of Quads consumed and fossil fuel fraction.

Logic for Constructing Scenarios for CO<sub>2</sub> Control Technology

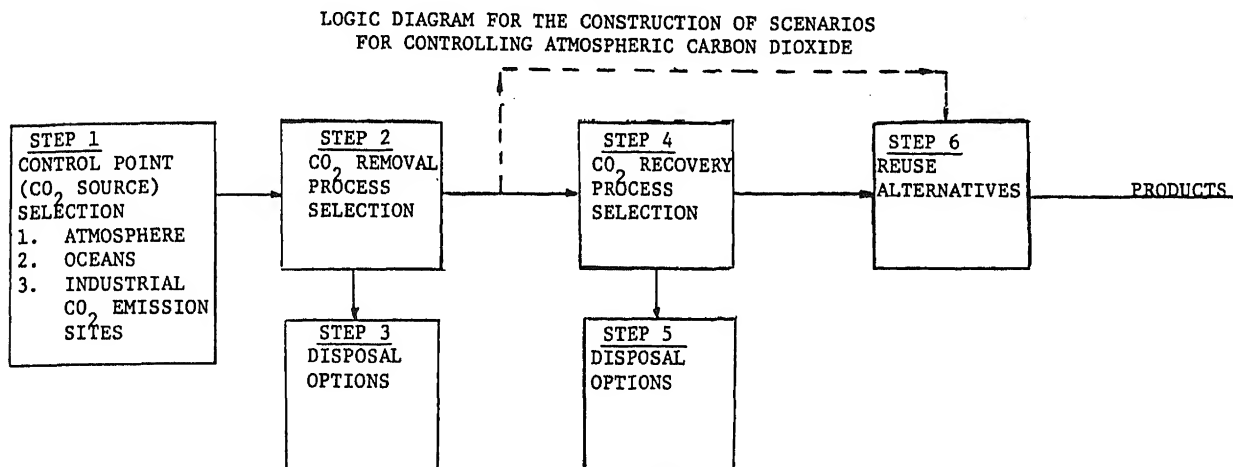
The suggested logic for guiding the construction of CO<sub>2</sub> control is shown in block diagram form in Figure 2.<sup>7</sup> The sequential steps to be followed are:

1. Control Point Selection - Three potential control points (CO



latter site has the advantage of providing a source of relatively high CO<sub>2</sub> concentration, while the former two provide more flexibility for site selection and simpler disposal or recovery and reuse logistics. A choice of control point limits the available choices of CO<sub>2</sub> removal processes and will reflect on the size of operation, the number of required sites, removal efficiency, energy requirements, the comparative economics and on the overall feasibility of operation.

Figure 2



A listing of options for the removal, recovery, disposal, and reuse of CO<sub>2</sub> as a function of control point is contained in Tables 5A through 5E.<sup>7</sup> Use of alternative fuels and energy sources are also considered as a potential means of controlling atmospheric CO<sub>2</sub>.

2. Removal Process Selection - Once a control point has been selected, the next task is to survey available removal processes to determine those which appear to be feasible, and compatible, with the selected control point

3. Identification of Disposal Alternatives for Captured CO<sub>2</sub> - This task involves the identification of alternatives which are available for disposal of the captured CO<sub>2</sub> (Step 2) directly, that is without going through a CO<sub>2</sub> recovery step, (e.g. desorption/sorbent regeneration). For example, if a naturally occurring, inexpensive and non-polluting CO<sub>2</sub> adsorbent was available the spent sorbent containing the captured CO<sub>2</sub> could be buried or stored in abandoned mine shafts rather than reused. A comparison between direct disposal versus CO<sub>2</sub> desorption/sorbent regeneration would be made at the time of scenario evaluation since each alternative would represent a separate scenario. For the case of CO<sub>2</sub> extraction by refrigeration or distillation, no desorption step is required.

4. CO<sub>2</sub> Recovery Process Selection - For a once through system, the quantity of sorbent consumed in absorbing or adsorbing CO<sub>2</sub> would generally be very large because of the vast quantities of CO<sub>2</sub> that would have to be effectively control the level of atmospheric

5. Identification of Disposal Alternatives for Recovered CO<sub>2</sub> - This task is similar to that described under Step 3, above, except that CO<sub>2</sub> would be in the form of a relatively pure gas, liquid or solid; that is, appreciable quantities of sorbents would not be present in the effluent (disposal) stream. Note that in the case of CO<sub>2</sub> extraction by refrigeration, liquid or solid CO<sub>2</sub> would be produced directly in the extraction step (Step 2) and therefore Steps 4 and 5 would not be required.

6. Identification of CO<sub>2</sub> Reuse Alternatives - The last step in the process of scenario construction involves exploring and identifying reuse possibilities for recovered CO<sub>2</sub> (Step 4). Several possibilities have been identified in Tables 5A through 5E. One option which has been given some consideration is to catalytically convert the recovered CO<sub>2</sub> to methanol by reaction with hydrogen using a non-carbonaceous energy source.<sup>6</sup> In some cases, it may be possible to proceed directly from CO<sub>2</sub> removal (Step 2) to CO<sub>2</sub> reuse as indicated by the broken line in Figure 2.

Since there are several key considerations in evaluating prospective control scenarios, e.g., energy and equipment requirements and sorbent property and losses, each scenario must be analyzed in some detail before realistic decisions can be made concerning its overall feasibility and comparative merits. A simplified approach could place emphasis on the wrong strategy and lead to false predictions and/or conclusions. However, the prime consideration in evaluating a CO<sub>2</sub> control system which derives its energy from a fossil fuel source is the energy required by the control system. In these cases, additional CO<sub>2</sub> would be generated in supplying energy to the control system and a point could be reached where more CO<sub>2</sub> is generated in supplying energy to the control system than is removed from the control point.

#### Carbon Dioxide Generation as a Function of Fuel and Energy Source

There is a gradation in the amount of carbon dioxide produced per unit energy released depending on the type of fuel or energy source used. Table 6 lists a number of sources of fuels, the heating values and the unit CO<sub>2</sub> generation in terms of mass of CO<sub>2</sub> generated per unit energy released (lb CO<sub>2</sub>/1000 BTU) in utilization of fuel.

It is noted that the least CO<sub>2</sub> generation per unit energy output is produced by natural gas and by hydrogen from reforming of natural gas. The next smallest amount of CO<sub>2</sub> released is from natural petroleum products i.e. oil and gasoline. Further increase in unit CO<sub>2</sub> is given by wood, alcohol, and benzene. This is followed by coal and coke.

## I. ATMOSPHERE

Absorption by Liquids

1. Water
2. Sodium carbonate
3. Potassium carbonate
4. Caustic
5. Amines (e.g. monoethanolamine and diethanolamine)
6. Other physical solvents (e.g. methanol and N-methylpyrrolidine)
7. Other chemical solvents (e.g. ammonia and Alkazid)
8. Combined physical and chemical absorbents (e.g. Sulfinol)
9. Physical a/o chemical solvents followed by caustic scrubbing

Adsorption by Solids

1. Naturally occurring sorbents (e.g. natural clays and zeolites)
2. Waste oil shale from retort operations
3. Molecular sieves

Extraction by RefrigerationIncreased Planting of Land Biota - photosynthesis

Absorption by Deep Ocean Waters - process used in conjunction with ocean thermal gradient power cycle.

Dilute Phase Methanation of Atmospheric CO<sub>2</sub> - hydrogen supplied by non-fossil energy source.

## II. OCEANS

Strip CO<sub>2</sub> with H<sub>2</sub>Distillation or Steam StrippingAcidification Followed by Degasification

## III. MAJOR INDUSTRIAL

CO<sub>2</sub> EMISSION

SOURCES (e.g.

fossil plant stacks)

Absorption by Liquids - same alternatives as for the atmosphere.

Adsorption by Solids - same alternatives as for the atmosphere.

Extraction by Refrigeration

Advanced Power Cycle - air separation followed by combustion of fossil fuels by oxygen. Recovery of CO<sub>2</sub> from combustion by above processes

Use of Alternative Energy Sources

OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT	OPTIONS FOR DISPOSAL OF CAPTURED CO <sub>2</sub>
I. ATMOSPHERE	<p><u>CO<sub>2</sub> Captured by Liquids</u></p> <ol style="list-style-type: none"> <li>1. Evaporate water, then bury residue-- carbonates and caustic sorbents only</li> <li>2. Deep oceans - water only</li> </ol> <p><u>CO<sub>2</sub> Captured by Solids</u></p> <ol style="list-style-type: none"> <li>1. Subterranean (e.g. abandoned mine shafts).</li> </ol> <p><u>CO<sub>2</sub> Captured by Refrigeration</u></p> <ol style="list-style-type: none"> <li>1. Extraterrestrial</li> <li>2. Deep oceans</li> <li>3. Antarctic region</li> <li>4. Subterranean</li> </ol> <p><u>CO<sub>2</sub> Captured by Plants</u></p> <ol style="list-style-type: none"> <li>1. CO<sub>2</sub> remains integral part of plant</li> </ol> <p><u>CO<sub>2</sub> Captured by Deep Ocean Waters</u></p> <ol style="list-style-type: none"> <li>1. Deep ocean</li> </ol>
II. OCEANS	<p><u>CO<sub>2</sub> Captured by Distillation</u></p> <ol style="list-style-type: none"> <li>1. Extraterrestrial</li> <li>2. Deep oceans</li> <li>3. Antarctic region</li> <li>4. Subterranean</li> </ol> <p><u>CO<sub>2</sub> Captured by Acid./Degas.</u></p> <ol style="list-style-type: none"> <li>1. Extraterrestrial</li> <li>2. Deep oceans</li> <li>3. Antarctic region</li> <li>4. Subterranean</li> </ol>
III. MAJOR INDUSTRIAL CO <sub>2</sub> EMISSION SOURCES (e.g. fossil plant stacks)	<p><u>CO<sub>2</sub> Captured by Liquids</u> - same alternatives as for atmosphere</p> <p><u>CO<sub>2</sub> Captured by Solids</u> - same alternatives as for atmosphere</p> <p><u>CO<sub>2</sub> Captured by Refrigeration</u> - same alternatives as for atmosphere</p> <p><u>CO<sub>2</sub> Removed by Adv. Power Cycle</u></p> <ol style="list-style-type: none"> <li>1. Extraterrestrial</li> <li>2. Deep oceans</li> <li>3. Antarctic region</li> <li>4. Subterranean</li> </ol>

Table 5C  
 OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE  
 OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT	OPTIONS FOR RECOVERING CAPTURED CO <sub>2</sub>
I. ATMOSPHERE	<p><u>CO<sub>2</sub> Captured by Liquids</u></p> <ol style="list-style-type: none"> <li>1. Desorption by flashing</li> <li>2. Desorption by distillation</li> <li>3. Strip with gases, i.e., H<sub>2</sub>, N<sub>2</sub>, steam, etc.</li> <li>4. Desorption by combined flashing and distillation or stripping</li> <li>5. Electrolytic decomposition of sodium carbonate to form sodium hydroxide, H<sub>2</sub>, O<sub>2</sub>, and CO<sub>2</sub> by non-fossil fuel source</li> </ol> <p><u>CO<sub>2</sub> Captured by Solids</u></p> <ol style="list-style-type: none"> <li>1. Decomposition by heating a/o stripping (e.g. by high pressure steam)</li> </ol> <p><u>CO<sub>2</sub> Captured by Methanation</u></p> <ol style="list-style-type: none"> <li>1. Absorb methane in a solvent, then desorb by flashing a/o distillation or stripping</li> </ol>
II. OCEANS	
III. MAJOR INDUSTRIAL CO <sub>2</sub> EMISSION SOURCES (e.g. fossil plant stacks)	<p><u>CO<sub>2</sub> Captured by Liquids</u> - same alternatives as for the atmosphere.</p> <p><u>CO<sub>2</sub> Captured by Solids</u> - same alternatives as for the atmosphere.</p> <p><u>CO<sub>2</sub> Captured by Refrigeration</u></p>

Table 5D

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE  
OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT



CONTROL POINT	OPTIONS FOR DISPOSAL OF RECOVERED CO <sub>2</sub>
I. ATMOSPHERE	<u>Gaseous CO<sub>2</sub></u> 1. Extraterrestrial  <u>Liquid CO<sub>2</sub></u> 1. Extraterrestrial 2. Deep oceans 3. Subterranean  <u>Solid CO<sub>2</sub></u> 1. Extraterrestrial 2. Deep oceans 3. Antarctic region 4. Subterranean
II. OCEANS	
III. MAJOR INDUSTRIAL CO <sub>2</sub> EMISSION SOURCES (e.g. fossil plant stacks)	

Table 5E

OPTIONS FOR THE REMOVAL, RECOVERY, DISPOSAL, AND REUSE  
OF CARBON DIOXIDE AS A FUNCTION OF CONTROL POINT

CONTROL POINT	REUSE ALTERNATIVES FOR CAPTURED/RECOVERED CO <sub>2</sub>
I. ATMOSPHERE	<p><u>Gaseous CO<sub>2</sub></u></p> <ol style="list-style-type: none"> <li>1. Catalytically convert CO<sub>2</sub> to gaseous a/o liquid carbonaceous fuels (methane, methanol, gasoline) by reaction with hydrogen, using non-fossil energy source (e.g. fission, fusion, solar)</li> <li>2. Decomposition of CO<sub>2</sub> to CO using non-fossil energy source (e.g. solar and nuclear radiation and high temperature heat), shift CO with water to form CO<sub>2</sub> and H<sub>2</sub>; subsequently convert to carbonaceous fuels</li> <li>3. React CO<sub>2</sub> with NH<sub>3</sub> to form urea fertilizer</li> <li>4. Use CO<sub>2</sub> for controlled photosynthesis in greenhouses--plant products in biosphere a/o burn for energy production</li> </ol> <p><u>Liquid CO<sub>2</sub></u></p> <ol style="list-style-type: none"> <li>1. Use for liquid CO<sub>2</sub> applications including industrial chemical uses</li> <li>2. Use for displacing crude oil from reservoir rock.</li> <li>3. Same alternatives as for gaseous CO<sub>2</sub> after vaporization</li> </ol> <p><u>Solid CO<sub>2</sub></u></p> <ol style="list-style-type: none"> <li>1. Use for dry ice applications</li> <li>2. Same alternatives as for gaseous CO<sub>2</sub> after sublimation</li> </ol>
II. OCEANS	
III. MAJOR INDUSTRIAL CO <sub>2</sub> EMISSION SOURCES (e.g. fossil plant stacks)	

Fuel Type	Chemical Formula	Heating Value BTU/lb	CO <sub>2</sub> generated lb CO <sub>2</sub> /lb fuel	CO <sub>2</sub> generated lb CO <sub>2</sub> /1000 BTU	Energy generated kwh(e)/lb CO <sub>2</sub> generated
Coke (ashless C)	C	14,100	3.67	0.26	
Bituminous Coal	CH <sub>0.8</sub> O <sub>0.1</sub>	13,000	2.75	0.21	0.56
Gasoline & Fuel Oil (petrol. dist.)	(CH <sub>2</sub> ) <sub>n</sub>	20,800	3.14	0.15	0.90
Benzene	C <sub>6</sub> H <sub>6</sub>	18,000	3.38	0.19	
Acetylene	C <sub>2</sub> H <sub>2</sub>	21,500	3.38	0.16	
Methanol (wood alc)	CH <sub>3</sub> OH	10,000	1.38	0.14	
Methanol (syn. from coal)	CH <sub>3</sub> OH	10,000	2.75	0.28	0.42
Biomass (wood, cellulose)	(CH <sub>2</sub> O) <sub>n</sub>	8,000	1.47	0.18	
Carbon Monoxide	CO	4,370	1.57	0.36	0.33
Natural Gas	CH <sub>4</sub>	24,100	2.75	0.11	1.07
SNG from coal gasification	CH <sub>4</sub>	24,100	8.75	0.34	1.01
SNG Coal & Nuclear Hydrogen	CH <sub>4</sub>	24,100	2.75	0.11	1.07
Hydrogen generated by:	H <sub>2</sub>	61,000	0	0	
Coal Gasification	H <sub>2</sub>	61,000	16.5	0.27	
Natural Gas Reforming	H <sub>2</sub>	61,000	7.0	0.11	
Nuclear-Electrolytic	H <sub>2</sub>	61,000	0	0	
Solar-Electrolytic	H <sub>2</sub>	61,000	0	0	
Geothermal-Electrolytic	H <sub>2</sub>	61,000	2.44	0.04	

Finally it is noted that synthetic natural gas (SNG made from coal) and carbon monoxide (CO) generates the largest amount of CO<sub>2</sub> per unit of energy released. Hydrogen produced by coal gasification generates less CO<sub>2</sub> than SNG from coal. In determining the CO<sub>2</sub> generated by synthetic fuels such as SNG, methanol and hydrogen from coal, the CO<sub>2</sub> generated in the production process is included. Thus, CO<sub>2</sub> generated from SNG (0.34) is 3 times greater than CO<sub>2</sub> generated from natural gas (0.11). Geothermal energy releases certain amounts of CO<sub>2</sub> per unit 1000 BTU which is estimated from a number of operating geothermal wells.<sup>10</sup> Of course there is no CO<sub>2</sub> generation if nuclear or solar energy is used to produce hydrogen fuel.

### Control Source CO<sub>2</sub> Concentrations

Table 7 lists the CO<sub>2</sub> concentration ranges of CO<sub>2</sub> sources and control points including, the atmosphere, the ocean, and the industrial emitters including natural wells used for energy sources. The concentration of CO<sub>2</sub> in the atmosphere and in the oceans are fairly constant around the globe. The concentration by weight in the atmosphere is about 5 times that in the ocean, however, because the ocean is about 1000 times denser than the atmosphere the total mass in a given volume in the ocean is about 200 times greater. The concentration of CO<sub>2</sub> in industrial emissions are about 10<sup>3</sup> to 10<sup>4</sup> times greater than that in the atmosphere. Thus, the energy required to



proportional to the logarithm of the volumetric source concentration, so that theoretically it should take 3 to 5 times more energy to extract CO<sub>2</sub> from the atmosphere than from stacks of fossil fueled plants. Because of other inefficiencies and frictional losses, the relative energy requirements increases much more than the logarithmic proportionality as the concentration of the source decreases.

Table 7

CO<sub>2</sub> CONCENTRATIONS AT CONTROL POINTS AND MINIMUM  
CO<sub>2</sub> SEPARATION ENERGIES

Control Point	CO <sub>2</sub> Concentration		Min. Separation Energy*
	% by Vol.	% by Wt.	kwh/lb CO <sub>2</sub>
Atmosphere	331x10 <sup>-4</sup>	502x10 <sup>-4</sup>	0.0570
Ocean	66x10 <sup>-4</sup>	100x10 <sup>-4</sup>	0.0570
Industrial Emitters			
Fossil Fueled Power Plants	7-20	11-28	0.0259-0.0179
Chemical Plants (lime, cement, NH <sub>3</sub> , coal gasif.)	20-100	28-100	0.0179-0.000
Metallurgical Plants (blast furnaces)	20	28	0.0179
Natural Gas Wells	0-50	0-73	0.0099
Geothermal Wells	~50	~66	0.0099

\* Minimum Energy based on free energy of mixing:

$\Delta F = RT \sum_i n_i \ln \frac{P_i}{P_i^0}$ , where  $P_i^0$  and  $P_i$  are the initial and final partial pressures of the  $i^{th}$  species, respectively. R is the gas constant, T is temperature in degrees absolute and  $n_i$  is the number of moles of the  $i^{th}$  species.

CO<sub>2</sub> Removal and Recovery Processes

a) The atmospheric and oceanic control points

Taking the atmosphere as the CO<sub>2</sub> control point one can estimate the amount of energy needed to remove and recover CO<sub>2</sub>. This has been done in a previous study<sup>6</sup> for a number of options. Results are summarized in Table 8.

Table 8  
ENERGY REQUIRED TO REMOVE AND RECOVER CO<sub>2</sub>  
FROM THE ATMOSPHERE AND SEA WATER<sup>6</sup>

<u>CO<sub>2</sub> Removal and Recovery Process</u>	<u>Energy for CO<sub>2</sub> Separation kwh(e)/lb CO<sub>2</sub></u>
1. H <sub>2</sub> O absorption/stripping (atm. pressure)	1.0
2. H <sub>2</sub> O absorption/stripping (20 atm)	9.7
3. Methanol adsorption/stripping (20 atm and -80°F)	7.3
4. Aqueous K <sub>2</sub> CO <sub>3</sub> absorption/stripping (atm pressure)	0.4
5. CO <sub>2</sub> adsorption/desorption	6.1
6. Cryogenic Separation	9.2
7. Caustic absorption/electrolytic stripping (isothermal process)	0.9
8. Stripping of sea water	0.4

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Note: For a bituminous coal burning power plant supplying power for removal of CO<sub>2</sub> in system 4 (aq. K<sub>2</sub>CO<sub>3</sub>), CO<sub>2</sub> generated/CO<sub>2</sub> removed = 0.4/0.56 = 0.71 and net CO<sub>2</sub> reduction/CO<sub>2</sub> removed = 1-0.71 = 0.29. At 100% CO<sub>2</sub> removal efficiency, net power plant efficiency would be reduced from 38% to 10%.

The most energy economic system is the dilute aqueous alkaline K<sub>2</sub>CO<sub>3</sub> system at atmospheric pressure because it has considerably higher solubility for CO<sub>2</sub> than water. An advanced isothermal system is also estimated using electrolytic decomposition of a carbonate-bicarbonate solution to release CO<sub>2</sub> and regenerate the alkaline carbonate solution to scrub the atmospheric CO<sub>2</sub>. The seawater stripping system has a low energy requirement because seawater

produced for a fossil fueled plant from Table 6, with the energy required to recover the  $\text{CO}_2$  shown in Table 8 one can estimate the ratio of  $\text{CO}_2$  produced to  $\text{CO}_2$  recovered. Thus, for all the processes listed in Table 8, with the exception of the aqueous  $\text{K}_2\text{CO}_3$  scrubbing and seawater stripping, more  $\text{CO}_2$  would be generated than recovered if a coal burning power plant were used to supply the electrical power. However, even in the  $\text{K}_2\text{CO}_3$  scrubbing case there is a significant penalty in energy generation efficiency. The conclusion to be reached here is that only a non-fossil fueled power plant such as nuclear or solar is allowable to generate the necessary electrical power for removal of  $\text{CO}_2$ , from the atmospheric and ocean control points.

#### b) The industrial control points

For the more concentrated industrial emission streams, less energy is required to recover the  $\text{CO}_2$ . Therefore, there is a larger margin for net  $\text{CO}_2$  recovery if fossil fuel is used to power the  $\text{CO}_2$  separation processes. However, estimates of energy requirements shown in Table 9 indicate that only for the high capacity solvent absorption/stripping processes (i.e.  $\text{K}_2\text{CO}_3$ , MEA, caustic scrub) are the energy requirements low enough to allow fossil fuel power plants to supply power for the separation process. However, even use of these high capacity solvents will tend to reduce power plant efficiency as indicated in note (3) of Table 9.

#### Disposal of $\text{CO}_2$

The removal and recovery of  $\text{CO}_2$  is only the first step in the environmental control chain. Disposal is probably the most critical step. Tables 5A through 5E lists a number of disposal schemes. The disposal breaks down into several ultimate possibilities.

##### 1. Burial in the deep ocean

In the two-box model, the world ocean is represented by two reservoirs, separated by a thermocline. One reservoir consists of surface layers to a depth of about 100 meters; the other, of deeper layers from the 100 meter depth to the ocean floor. Mixing is assumed to occur rapidly within each box or reservoir, but exchange between the two boxes proceeds slowly. Thus, the deep ocean represents a sink for  $\text{CO}_2$  since there is no direct exchange between the atmosphere and the deep ocean. The main discrepancy between the simple two-box model and the real ocean is that in some regions (e.g. Arctic, Antarctic and Gibraltar regions) convection currents extend from the ocean surface to the ocean bottom.

One proposal for disposing of collected  $\text{CO}_2$  is to inject it into the sea at the Strait of Gibraltar.<sup>4</sup> Presumably, the current would carry it to the deeper ocean waters where it would remain for centuries. Another proposal is to inject liquid  $\text{CO}_2$  into the deep sea at a density greater than that of deep sea water via a long pipe. The  $\text{CO}_2$  would sink to the bottom of the ocean forming a liquid  $\text{CO}_2$  lake within the ocean.

<u>CO<sub>2</sub> Removal and Recovery Process</u>	Energy for CO <sub>2</sub> Separations	
	<u>kwh(e)/lb CO<sub>2</sub><sup>(2)</sup></u>	
1. Aqueous K <sub>2</sub> CO <sub>3</sub> absorption/stripping	0.1	<sup>(3)</sup>
2. Caustic absorption/electrolytic stripping (isothermal process)	0.2	
3. Amine absorption/stripping	0.1	
4. Adsorption/desorption on molecular sieves	0.6	
5. Cryogenic Separation	1.8	
6. Absorption in sea water <sup>(1)</sup>	0.6	<sup>(1)</sup>

Note:

- (1) @60% CO<sub>2</sub> removal efficiency and including deep ocean disposal of captured CO<sub>2</sub>
- (2) For coal burning plant energy output per unit CO<sub>2</sub> generated is 0.56 kwh(e)/lb CO<sub>2</sub>; any removal system requiring values equal to or greater than this yields no reduction in net CO<sub>2</sub> emitted.
- (3) For a K<sub>2</sub>CO<sub>3</sub> removal system (process 1), the overall power plant efficiency would be affected as follows:

<u>CO<sub>2</sub> Removal Efficiency - %</u>	<u>Net Power Plant Efficiency - %</u>	<u>Lb CO<sub>2</sub> Discharged To Atmosphere Per Net kwh(e) Generated</u>
100	31.0	0
85	32.0	0.33
75	33.5	0.52
60	33.8	0.82
50	34.5	1.01
25	36.3	1.44
0	38.0	1.83

The current release rate of fossil carbon to the atmosphere is about  $5 \times 10^{15}$  g/yr, whereas the current carbon content of the deep ocean is estimated at  $0.373 \times 10^{20}$  g. Therefore, if all of this fossil carbon was collected and deposited in the deep ocean, the quantity of carbon contained therein would increase by about 0.013% per year.

by equilibrating a high CO<sub>2</sub> concentration on natural zeolite, is of main concern with this method of disposal.

### 3. Extraterrestrial burial

CO<sub>2</sub> packaged as solid, liquid or high pressure gas would be sent by rocket beyond the escape velocity of the earth or possibly to other planets. In this way one can assure that the CO<sub>2</sub> would not gravitate back to earth. If non-fossil generated hydrogen is used as rocket fuel no exhaust CO<sub>2</sub> penalty would be incurred, however, energy costs would be excessive.

### 4. Recycle in products

Although a number of CO<sub>2</sub> containing commercial products can be made for the economy, i.e. dry ice, soda ash, inorganic carbonates, urea, the CO<sub>2</sub> remains about the same because fossil energy is used to produce them and the markets for the products are limited.

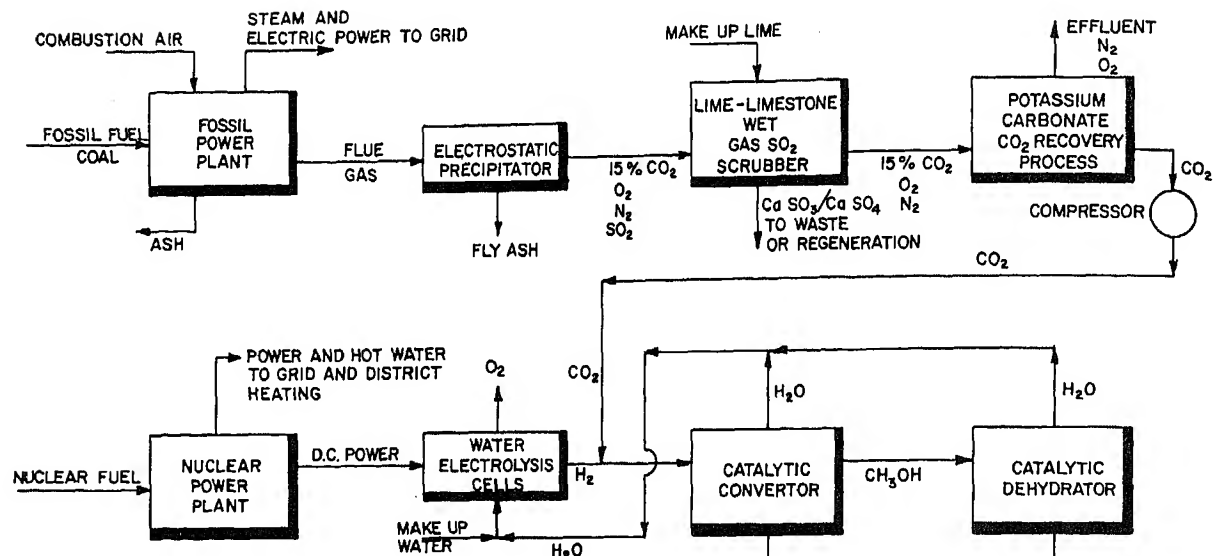
A unique disposal method is to convert the recovered CO<sub>2</sub> to synthetic liquid and gaseous carbonaceous fuel using a non-fossil energy source, for example, nuclear power. In this way, the CO<sub>2</sub> can be reused thus reducing the CO<sub>2</sub> buildup in the atmosphere. There are several options in applying this carbon-nuclear cycle.<sup>8,9</sup>

(a) Coal can be converted to SNG, oil, and gasoline using nuclear power based electrolytic hydrogen. The nuclear hydrogen would be used directly to hydrogenate the coal. In this manner the CO<sub>2</sub> buildup would be reduced by a factor of 3 compared to the natural gas and petroleum cases.

(b) Remove and recover CO<sub>2</sub> from coal burning power plants and combine with nuclear electrolytic hydrogen to produce methanol which can be dehydrated to gasoline on zeolite catalysts.<sup>11</sup> Figure 3 shows a flowsheet of the system. In this manner, power is produced from the fossil plant and the carbon in the CO<sub>2</sub> reused in producing synthetic carbonaceous fuel.

(c) Remove and recover CO<sub>2</sub> from the atmosphere and combine with electrolytically produced hydrogen to form synthetic carbonaceous fuels. A flowsheet of the system is shown in Figure 4 and features a novel isothermal (electrolytic) system for regenerating the CO<sub>2</sub> and caustic scrub solution in addition to the product hydrogen.

A quantitative estimate of the number of nuclear reactors needed to convert the CO<sub>2</sub> emissions from industrial stack emissions to synthetic carbonaceous fuels for the transportation sector in the US is shown in Table 10.<sup>8</sup> The data indicates that there is more than enough CO<sub>2</sub> emitted from fossil energy power plants to supply the needs of the automotive industry and that about one thousand 1000 MW(e) nuclear reactors would be needed to make the total conversion.



REACTIONS:

POTASSIUM CARBONATE CO<sub>2</sub> RECOVERY PROCESS  
 $\text{CO}_2 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{KHCO}_3$

ELECTROLYSIS  
 $3\text{H}_2\text{O} \rightarrow 3\text{H}_2 + \frac{3}{2}\text{O}_2$

CATALYTIC CONVERTOR  
 $3\text{H}_2 + \text{CO}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$

CATALYTIC DEHYDRATION  
 $n\text{CH}_3\text{OH} \rightarrow (\text{CH}_2)_n + n\text{H}_2\text{O}$

A potential large scale use for CO<sub>2</sub> is in tertiary treatment of depleted oil wells, however, this application may be of limited value as a long term disposal method. Another recycle system is to utilize the CO<sub>2</sub> as a diluent with oxygen in a fossil fuel power plant so that the only effluent is CO<sub>2</sub> thus reducing energy requirements for removal and recovery. With this system a compact highly efficient power plant can be designed. The plant can be sited in highly populated areas and the CO<sub>2</sub> removed for disposal in remote areas.

Finally, an all nuclear or solar-electric hydrogen economy would essentially reduce CO<sub>2</sub> emissions to a negligible level.

# FROM NUCLEAR POWER, AIR AND WATER

## FIXATION OF ATMOSPHERIC CARBON

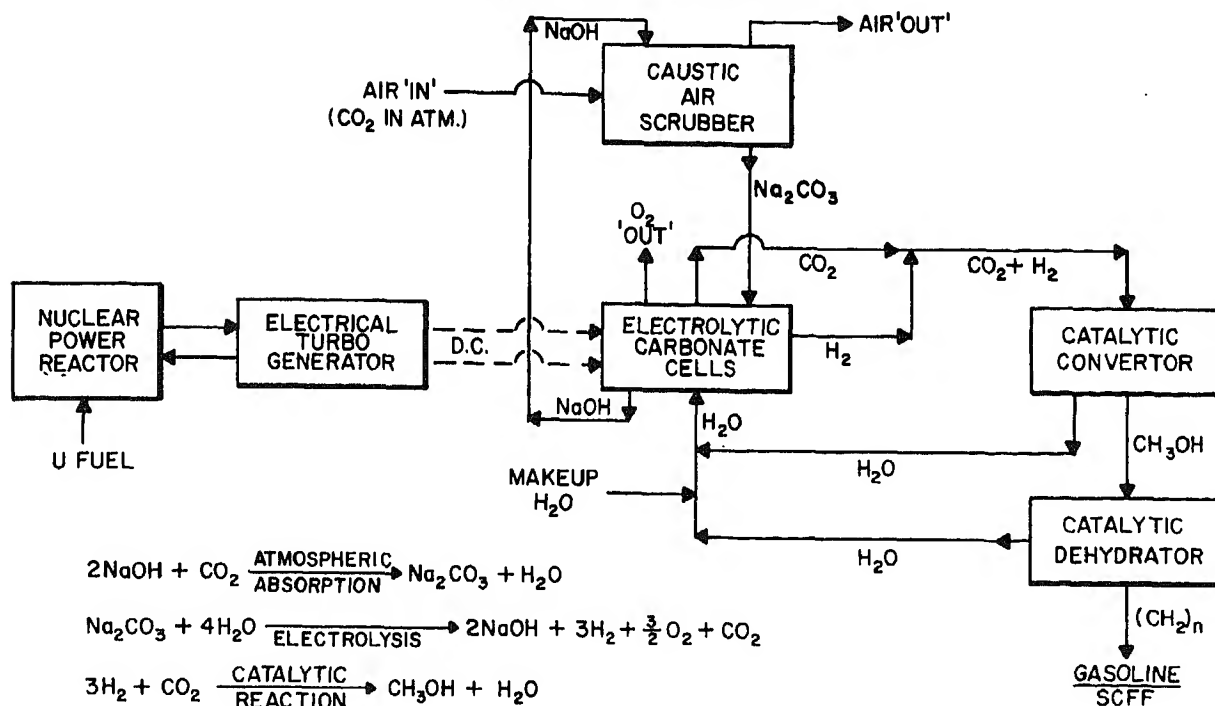


Table 10

INDUSTRY RESOURCE CAPACITY TO PRODUCE SYNTHETIC CARBONACEOUS FUELS  
AND FEEDSTOCKS FROM EFFLUENT CO AND CO<sub>2</sub> FEEDSTREAMS AND NUCLEAR POWER<sup>9</sup>

Based on 1975 Production Capacities

Industry	Production capacity Millions tons/yr	CO <sub>2</sub> or CO availability Millions tons/yr	Gasoline production capability Billions gal/yr	No. of 1000 MW(e) nuclear power plants required
Lime and Cement	25 Lime 85 Cement	86 CO <sub>2</sub>	9	90
Steel	125 Steel	125 CO	20	125
Coal for Power	500 Coal	1,560 CO <sub>2</sub>	165	1,680
Gasoline, US Consumption		(945 CO <sub>2</sub> ) <sup>(1)</sup>	100	(1,000) <sup>(1)</sup>

<sup>1)</sup> Capacity needed to meet 1975 US consumption of gasoline of approximately 100 billion gal/yr.

growing global technological population, the following measures can be recommended.

- (1) Attempt to find and utilize more natural gas (and petroleum) in preference to coal because of its 2 to 3 times lower CO<sub>2</sub> emissions per unit energy produced.
- (2) Consider recovering the more concentrated CO<sub>2</sub> industrial stack gas emissions using fossil fuel power.
- (3) Attempt recovering the less concentrated atmospheric and oceanic CO<sub>2</sub> using nuclear power or another non-fossil power source such as solar.
- (4) Consider disposal of the CO<sub>2</sub> by deep ocean burial.
- (5) Combine coal with nuclear electrolytic hydrogen to produce SNG.
- (6) Produce synthetic carbonaceous fuel from atmospheric CO<sub>2</sub> and nuclear electrolytic hydrogen.
- (7) Convert to a hydrogen economy using a non-fossil energy source.
- (8) Convert to an all electrical economy substituting nuclear or another non-fossil fuel source such as solar.
- (9) Convert to a biomass - photosynthetic energy economy.

Since no energy source is truly benign, in the long run, the realistic ECT scenario for CO<sub>2</sub> will depend on the lesser of the evils in selecting and utilizing our energy source alternatives.

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## 1. INTRODUCTION

If we burn fossil fuels at too rapid a rate in the future, there is a real threat of unacceptable consequences from increasing levels of atmospheric carbon dioxide. While the uncertainties involved are large, there are ample reasons for concern:

Atmospheric carbon dioxide is increasing.

The rate of fossil fuel consumption has increased exponentially for 120 years.

The reserves of fossil carbon are very large.

The oceans can take up carbon dioxide from the atmosphere at only a limited rate.

The magnitude of the greenhouse effect may be several degrees Celsius per doubling of atmospheric carbon dioxide.

If we do not limit the rate of fossil fuel consumption in the future, it seems essential to consider, as Dr. Steinberg has outlined in his paper, possible means of controlling the excess carbon dioxide produced.

The goal of our study, which is still underway, has been to examine in more detail the technical feasibility, monetary cost and energy cost of some of the more promising means of capture and disposal. Specifically we have restricted ourselves to the collection of carbon dioxide from stationary sources such as power plants, though these amount to only 20 to 30% of the total fossil carbon dioxide flux, and the only means of disposal we have considered in any detail is ocean disposal.

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\*Research sponsored by the Division of Environmental Control Technology, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

gas by present technology have been estimated by Pappano et al. (1976) and by Rump et al. (1977) for large scale operations (in the later case, 270 metric tons of CO<sub>2</sub>/hr) for enhanced oil recovery. In Table I, these energy costs are compared with the energy worth of the carbon dioxide, i.e., the energy derived by burning the coal that produced it. We have assumed a coal (Sewanee Coal from Grundy Co., Tenn.), one metric ton of which produces 6.79 million kcal of heat and 2.55 metric tons of carbon dioxide. This gives a cost of CO<sub>2</sub> recovery that is about 46% of the energy worth. The dollar cost is estimated at about \$19 per metric ton of CO<sub>2</sub> (\$1.80/million BTU).

The estimated energy cost of compression to 150 atm and transporting 25 miles are small by comparison. The estimated energy costs of conversion into solid forms such as dry ice or the hydrate are more appreciable, 14 to 18% of the energy worth of the carbon dioxide. The dollar costs of these steps are proportionately higher because much of the energy consumed is electrical.

TABLE I. COST OF COLLECTING AND PROCESSING CO<sub>2</sub> FROM STACK GAS

	$\frac{10^6 \text{ kcal}}{\text{Metric Ton of CO}_2}$	% of CO <sub>2</sub> <sup>b</sup> Energy Worth	\$/Metric Ton of CO <sub>2</sub>
Capture of CO <sub>2</sub> <sup>a</sup>	1.23	46	19
Compress to 150 atm, <sup>a</sup> Transport 40 km	0.10	4	4
Solidify CO <sub>2</sub> <sup>c</sup>			
To Dry Ice	0.36	14	14
To CO <sub>2</sub> ·6H <sub>2</sub> O	0.47	18	17

<sup>a</sup>Rump et al. (1977). 290 metric tons CO<sub>2</sub>/hr, MEA process.

<sup>b</sup>One metric ton of coal assumed to yield 6.79·10<sup>6</sup> kcal and 2.55 metric tons of CO<sub>2</sub>.

<sup>c</sup>Calculated from data of Stickney (1932).

### 3. COMBUSTION IN OXYGEN

Marchetti (1978) has suggested that coal be burned in pure oxygen to produce nearly pure carbon dioxide and water, thus avoiding the costly collection from flue gas. Table II summarizes the comparable costs of this alternative.

Preparation of Pure Oxygen <sup>a</sup> (22 atm)	0.76	29
Increase in Plant Efficiency (38% to 42%)	<u>-0.28</u>	<u>-11</u>
Net Cost	0.48	18
Capture CO <sub>2</sub> From Stack Gas	1.23	46

<sup>a</sup>From data supplied by P. Koster, Linde Div., Union Carbide Corp.

The major cost is, of course, the separation and compression of oxygen from air, amounting to 400 kWh of mostly electrical energy per metric ton of oxygen. Since 2.15 metric tons of oxygen are required to burn one metric ton of our coal, this amounts to 1.95 million kcal/metric ton of coal (assuming 38% efficiency for the production of the electricity). Thus the oxygen production costs amount to 0.76 million kcal/metric ton of CO<sub>2</sub>, considerably less than the cost of recovering CO<sub>2</sub> from normal flue gas.

Moreover, it is reasonable to expect there will be an increase in plant efficiency from (1) the reduction in heat loss to the stack gas, (2) the elimination of the combustion air fans, (3) perhaps an increase in combustion temperature. If an improvement in overall efficiency from 38% to 42% were possible, this would amount to 0.28 million kcal/metric ton of CO<sub>2</sub> which could be credited against the production costs of the oxygen.

An additional possible advantage of combustion in pure oxygen is that there may be no need for an SO<sub>2</sub> scrubbing step which otherwise would precede the CO<sub>2</sub> scrubber. The CO<sub>2</sub> and SO<sub>2</sub> could be compressed and disposed of together.

#### 4. OCEAN DISPOSAL

If carbon dioxide can be delivered to the deep oceans this would give a retention time of the order of a thousand years even if this acidic gas did not react with the basic minerals present such as calcium carbonate. We will consider various forms of carbon dioxide that would be denser than seawater and have a vapor pressure lower than the hydrostatic pressure at the depth of injection.

increases the density. The apparent molar volume of dissolved  $\text{CO}_2$  (measured before the turn of this century and cited by Eley, 1939) is about  $35 \text{ cm}^3$ . The density increase at the maximum solubility is only about 1%, however, not enough to exceed the density of seawater. Hence fresh water does not seem suitable as a medium for the disposal of carbon dioxide in the ocean.

TABLE III. THE  $\text{CO}_2$  CONTENT AND DENSITY OF WATER AT  
THE LIQUEFACTION PRESSURE OF  $\text{CO}_2$

Temp. (°C)	Vapor Pres. of Liq. $\text{CO}_2^a$ (atm)	Dissolved $\text{CO}_2^b$ (Moles/kg $\text{H}_2\text{O}$ )	Conc. <sup>b</sup> (Wt %)	$\frac{\rho(\text{Sol'n})^c}{\rho(\text{H}_2\text{O})}$
0	34.4	1.45	6.02	1.0125
5	39.1	1.36	5.64	1.0117
10	44.4	1.29	5.37	1.0111
15	50.2	1.25	5.22	1.0108
20	56.5	1.24	5.16	1.0106
25	63.5	1.25	5.22	1.0108
30	71.2	1.29	5.39	1.0111

<sup>a</sup>Vukalovich and Altunin (1968), p. 97.

<sup>b</sup>Based on data in Linke (1958), p. 460.

<sup>c</sup>Calculated assuming the molar volume of dissolved  $\text{CO}_2$  is  $35 \text{ cm}^3$ .

#### 4.2 Carbon Dioxide in Seawater

The solubility of carbon dioxide in seawater as a function of pressure up to the liquefaction pressure at various temperatures is shown in Fig. 1. Assuming conservatively that the molar volume is no larger in seawater than it is in fresh water, there should be a substantial density increase, for example,  $0.0075 \text{ g/cm}^3$  at a concentration of 1 mole/kg. The minimum depth of injection without the formation of bubbles is shown on the upper scale.

To consider further the disposal of carbon dioxide in seawater, let us imagine the simple system shown in Fig. 2: Water is taken in at a temperature of  $t_1$  and density  $\rho_1$  which depend on the location and depth chosen; it is pumped through a gas-liquid contactor where  $\text{CO}_2$  is dissolved to a concentration  $C$ , the density rises to  $\rho_3$  and because of the heat of solution the temperature

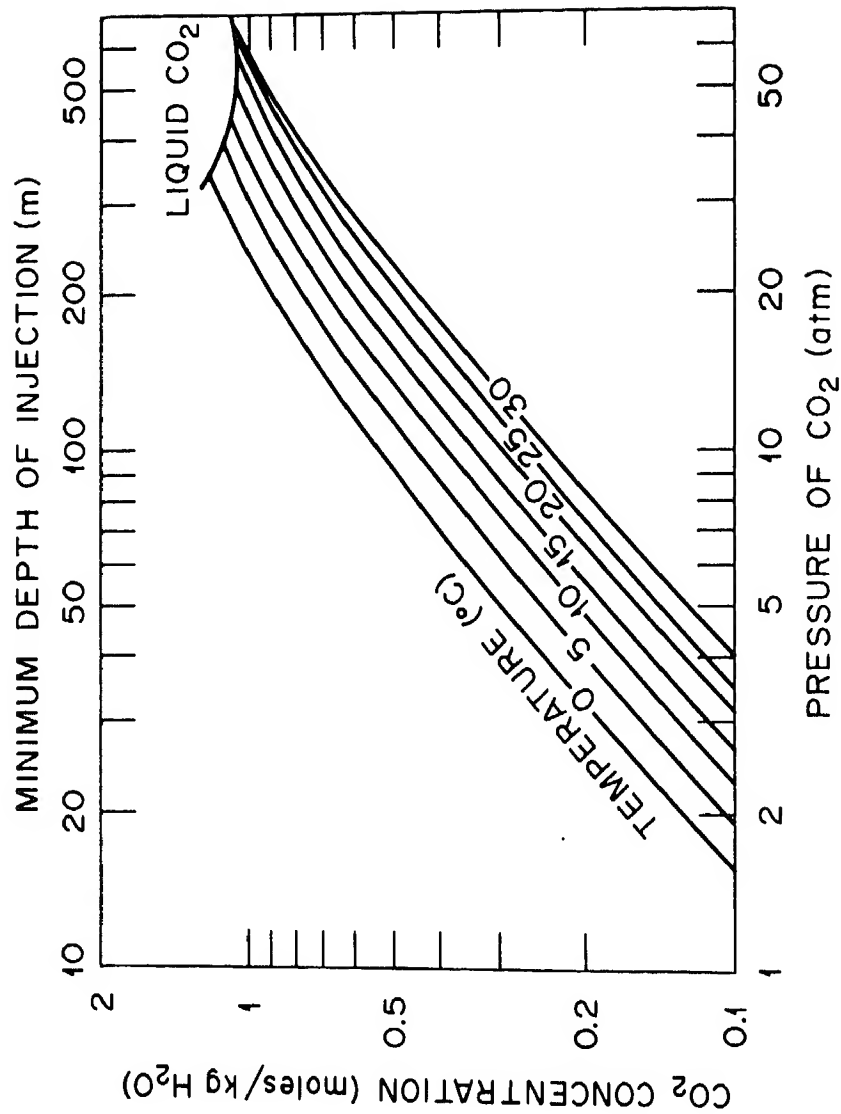


Fig. 1. Solubility of CO<sub>2</sub> in Seawater

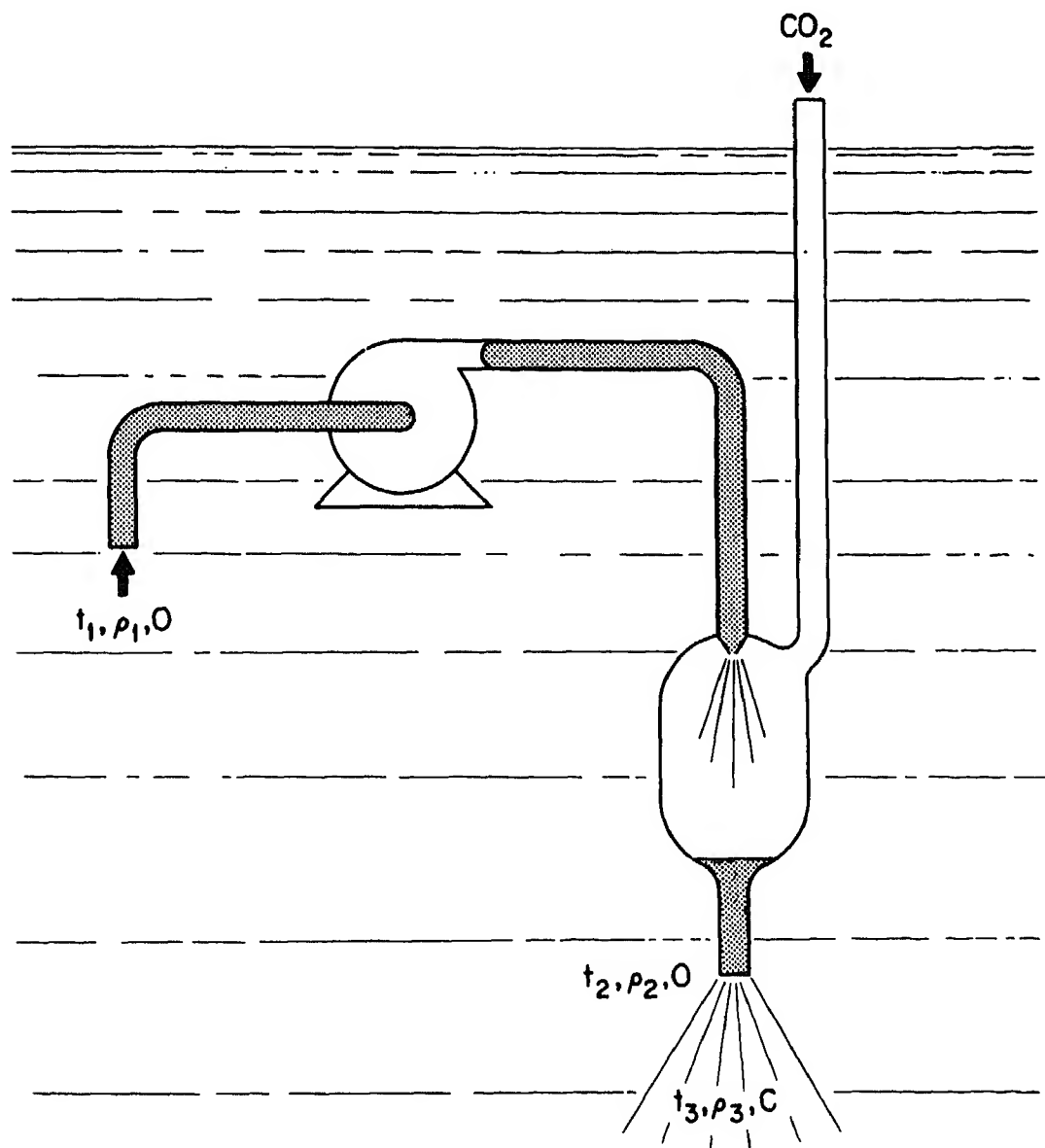


Fig. 2. Schematic Representation of the Injection of CO<sub>2</sub> into Seawater

$$t_3 = t_1 + 5 \cdot C ,$$

(1)

based on a heat of solution of 5 kcal/mole. The density difference at the outlet,  $\rho_3 - \rho_2$ , can be calculated as the sum of two terms.

$$\rho_3 - \rho_2 = [\rho(t_3, 0) - \rho(t_2, 0)] + [\rho(t_3, C) - \rho(t_3, 0)] .$$

(2)

The first is the density decrease caused by heating the ambient seawater from  $t_2$  to  $t_3$ , known accurately from data for seawater. The second term is the density increase produced by introducing the carbon dioxide to a concentration of  $C$  moles/kg, and can be estimated from the approximation

$$\rho(t_3, C) - \rho(t_3, 0) \approx 0.0072 \cdot C ,$$

(3)

based on a molar volume of  $35 \text{ cm}^3$ .

It turns out that the density difference,  $\rho_3 - \rho_2$ , which we wish to maximize depends on two quantities, the inlet temperature  $t_1$  (which should be minimized) and the concentration of carbon dioxide  $C$  (which should be maximized). The calculations plotted in Fig. 3 were done assuming the injection point was at the bottom of the thermocline ( $\sim 1,000$  m depth) where the water temperature becomes approximately constant below  $5^\circ\text{C}$ . Injection at lesser depth would give larger density differences because the ambient water temperature is higher.

One of our early ideas for the disposal of carbon dioxide from a coal-fired power plant was to take advantage of the cooling-seawater requirements of an ocean thermal energy conversion (OTEC) plant. A 1,000 MW(e) coal-fired plant produces about 210 kg/sec of carbon dioxide. If this were dissolved in seawater to a concentration of 0.5 moles/kg, about 10,000 kg/sec of water flow would be required. A 100 MW(e) OTEC plant proposed by TRW Inc. would require 380,000 kg/sec of cooling water. This is 38 times the flow rate required to dissolve the  $\text{CO}_2$  released by a 1,000 MW(e) fossil fuel plant, and we thus conclude that there would be no advantage in using the OTEC plant. The same benefit could be gained by siting the fossil plant on a floating platform or at a coastal location where the  $\text{CO}_2$ -seawater solution could be discharged at the proper depth. Indeed the seawater requirements for such disposal are so modest that if deep ocean water were used for cooling the condenser of a coal-fired plant, it could carry away all the carbon dioxide produced by the plant at a concentration of the order of 0.1 moles/kg while at the same time offering greater thermal efficiency because of its lower temperature.

#### 4.3 Carbon Dioxide Hydrate

The hydrate of carbon dioxide has a clathrate structure (Miller and Smythe, 1970) with a density of about  $1.12 \text{ g/cm}^3$ , greater than that of seawater. If large blocks of the solid were dropped into the sea they would sink rapidly.



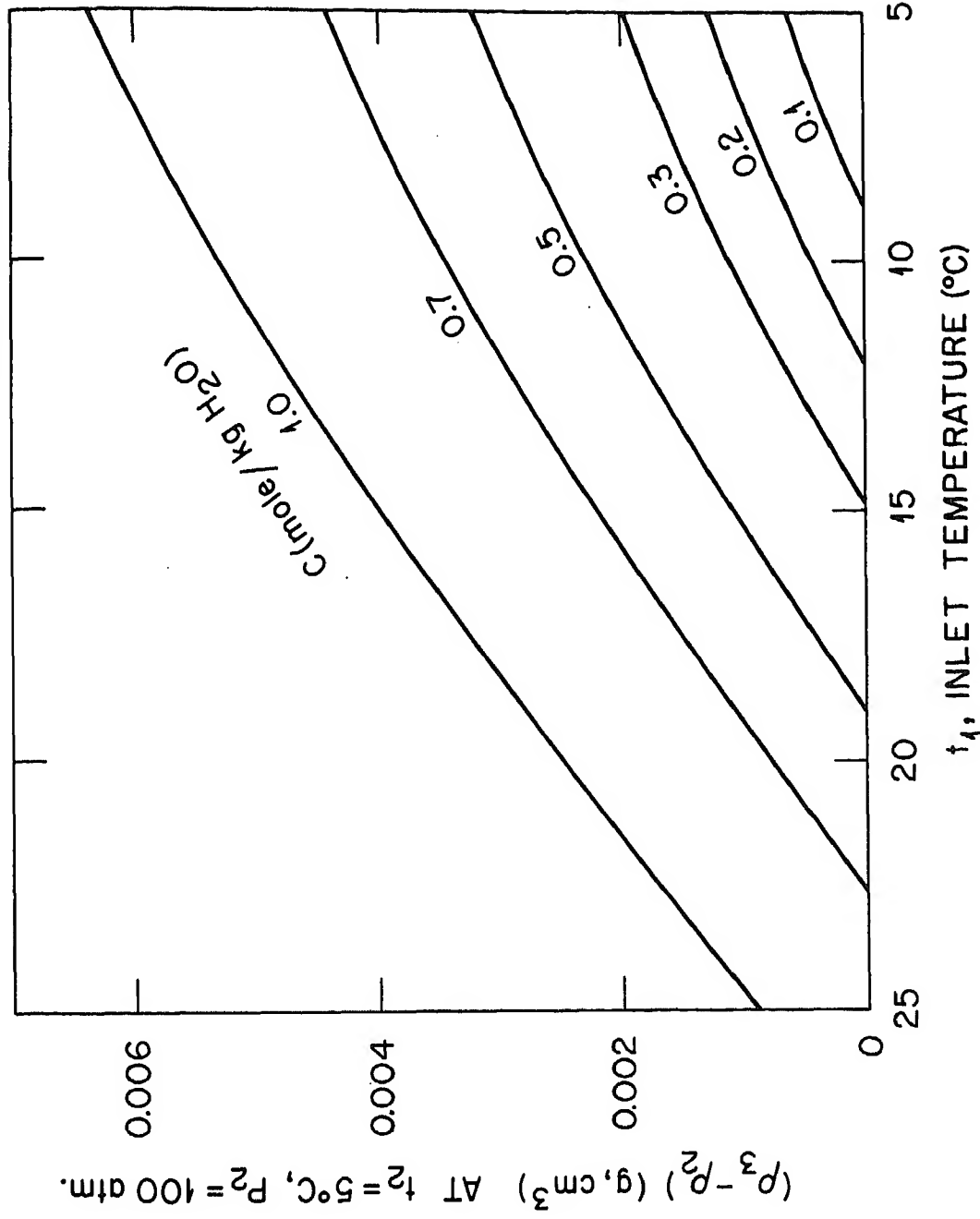


Fig. 3. The Excess Density of a  $\text{CO}_2$  Disposal Stream in Seawater

formation would cease. The reaction product thereafter would be a carbon dioxide-seawater solution more dense than the surrounding water. The reaction rate might be slow enough to permit the block to reach the bottom before an appreciable fraction had been consumed.

#### 4.4 Liquid Carbon Dioxide

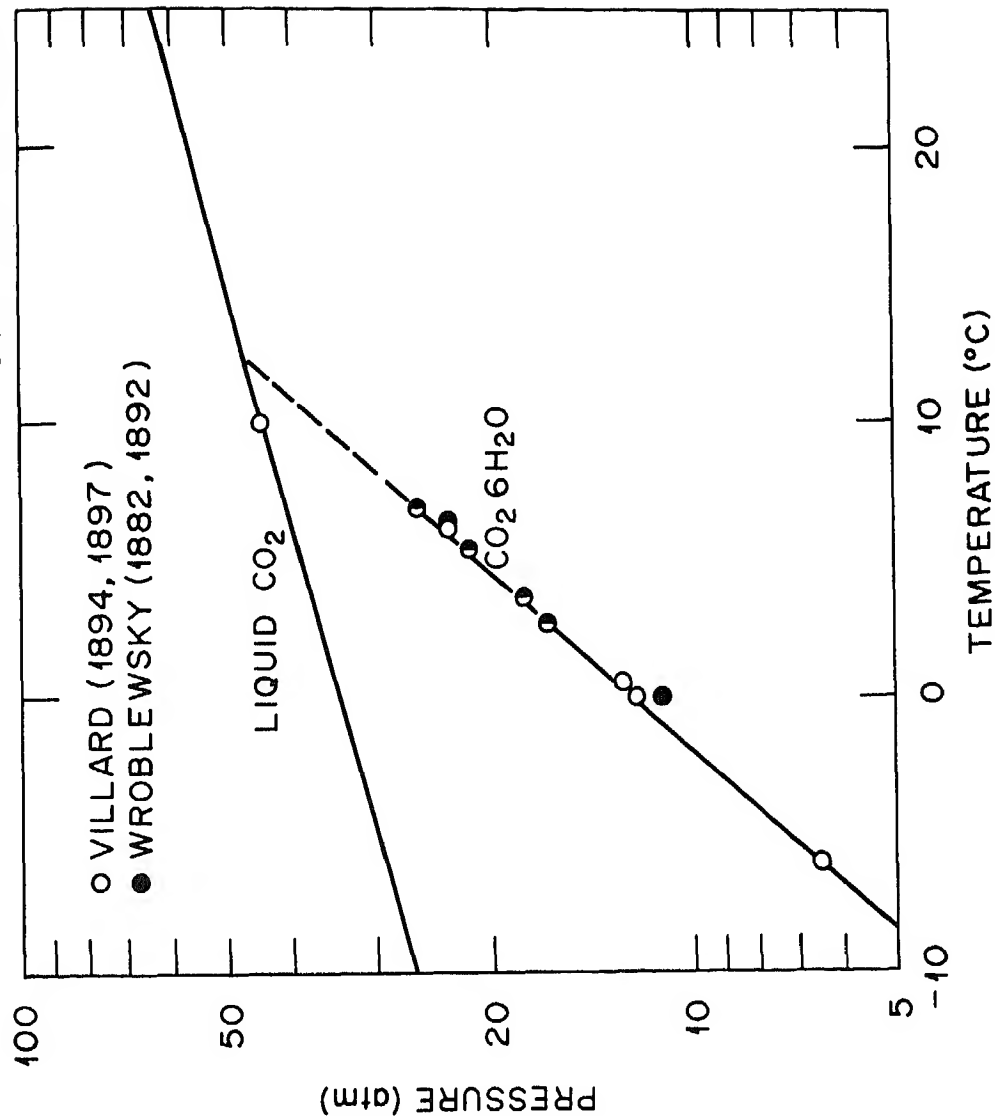
Marchetti (1976) has mentioned a suggestion of Nordhaus for disposal in the form of liquid carbon dioxide. In Fig. 5 we see that while the density of the liquid is less than that of seawater at the surface, it is much more compressible and has a much higher thermal coefficient of density. From these curves it appears, however, that a considerable depth of injection would be necessary, about 3,000 meters, to insure that the  $\text{CO}_2$  is more dense than the surrounding seawater.

#### 4.5 Dry Ice

This form has the greatest density, about  $1.5 \text{ g/cm}^3$ , and would be the most economical to transport by water. Large blocks of it would sink rapidly and, again, once past a depth of about 500 m, bubbling should cease and the reaction products - the hydrate, the liquid and dissolved  $\text{CO}_2$  - should be denser than the surrounding water. This form of carbon dioxide might survive the trip to the ocean bottom best of all.

### 5. SUMMARY AND CONCLUSION

1. The cost of  $\text{CO}_2$  recovery from flue gas will be high.
2. Combustion of fuel in pure oxygen may permit a more efficient recovery of  $\text{CO}_2$  (and  $\text{SO}_2$ ).
3. Deep ocean disposal would give a long retention time.
4. Fresh water is not a suitable medium for ocean disposal.
5. Seawater could be used because dissolving  $\text{CO}_2$  should increase the density of seawater.
6. The cooling water flow from one OTEC plant could accommodate the  $\text{CO}_2$  output of hundreds of fossil fuel plants of the same capacity.
7. The cooling water flow from a fossil fuel plant is more than adequate to accommodate the  $\text{CO}_2$  output of the plant, but the plant must be sited to permit ocean disposal.
8. We need more data on the density effect of introducing  $\text{CO}_2$  into seawater as a function of temperature and pressure.



Vap Pressure of Liquid CO<sub>2</sub> and CO<sub>2</sub> Hydrate

Fig. 4. Vapor Pressure of Liquid CO<sub>2</sub> and CO<sub>2</sub> hydrate. Data Cited by Quinn and Jones (1936)

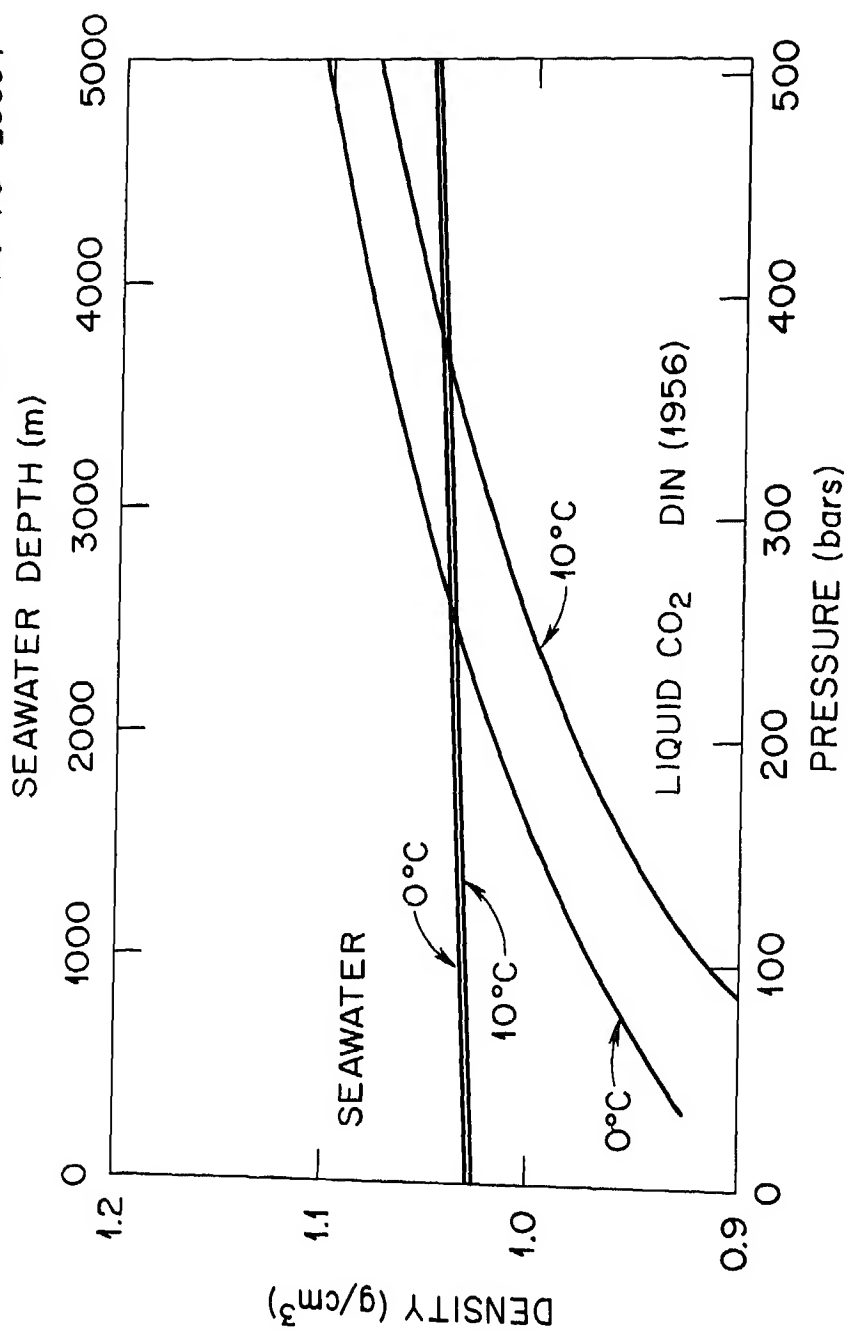


Fig. 5. A Comparison of the Densities of Liquid CO<sub>2</sub> and Seawater

ice.

11. Liquid CO<sub>2</sub> might be used for ocean disposal, but the depth of injection would be over 3,000 m.

#### ACKNOWLEDGMENT

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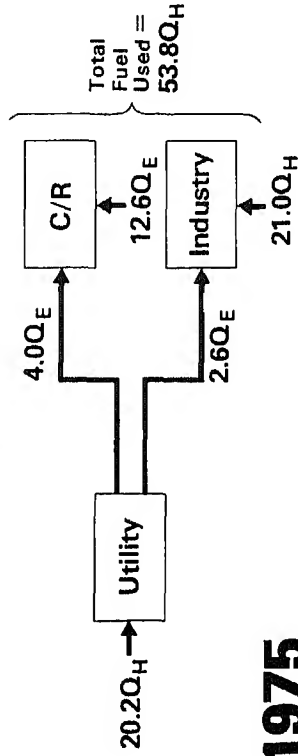
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Cogeneration is classically thought of as a conservation technique. What is perhaps less appreciated is the fact that cogeneration is also a technique for the reduction of emissions. This is one of the benefits of a cogeneration system since less fuel is burned to produce electrical power and process heat than in isolated powerplants or furnaces. Despite these benefits, there is concern that if cogeneration becomes widespread in the US on the scarce fuels of today (natural gas and light distillate petroleum) it could potentially displace the coal required by utility power generation and increases our imports of scarce fuels. If that can foreseeably happen, and the US balance of payments to foreign countries were to increase, then very reasonable arguments can be made that cogeneration should not proceed without regard for the systems' potential for switching to fuels from far more abundant sources-like coal and coal-derived fuels. The author's position is not necessarily one of announcement of DOE policy but it is very much one of advocacy for cogeneration and the development of engine technology that can operate reliably and cleanly on fuels from coal at dispersed sites with the potential for utility ownership. Very direct benefits that this will permit are (1) the reduction of national consumption of scarce petroleum and natural gas to help the US balance of payments problem, (2) big increases in national coal production requirements, and (3) reduction in the amount of fuel required to make both electricity and process heat by factors ranging from 20 to 40% for the purposes of emission reductions on minimally processed coal-derived fuels, (4) keeping the cost for fuel burned in an operation from rising due to increased costs/BTU on coal-derived fuels and (5) dispersed power generation should reduce national vulnerability to disaster of one form or another.

To give the reader some indication of how large the opportunity is for coal in cogeneration systems to meet the country's growing electrical and heat demands, refer to Figure 1. This shows a current and projected schematic of how energy is used in our two stationary sectors (commercial/residential and industrial) and how it is supplied by the purchase of fuel and the purchase of electricity from a utility company. In the year 2000, a projection of how heat and electrical requirements might be met with and without cogeneration is shown. Cogeneration is shown in the schematic to be used to meet national electricity growth requirements of nearly 8 quads electric between 1975 and 2000, with some recovered on-site waste engine heat being used to displace fuel that would otherwise be burned for process heat in these two sectors. While the overall national energy savings are only 5.3 quads/year, the new market for fuel burned in engines in cogeneration systems in this upper bound scenario is 25.3 quads/year. If heat engines and fuels from coal can be developed to meet this market and its constraints (technical, environmental and cost) then this can be considered as a market for coal rather than scarce fuels. Note that this 25.3 quad/year market by 2000 is in addition to the current 20.2 quad/year fuel requirement of utilities.

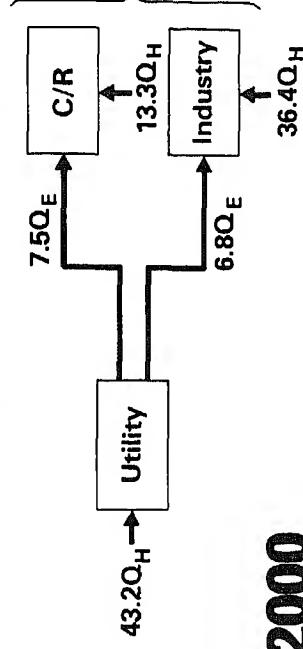
# The Opportunities for Coal Cogeneration in the New Market - Year 2000

## No Cogeneration



1975

## No Cogeneration



2000

## Symbols and Notes

$Q_H$  = Quads Fuel Burned/Year

$Q_{WH}$  = Quads Waste Heat Recovered in Cogen/Year

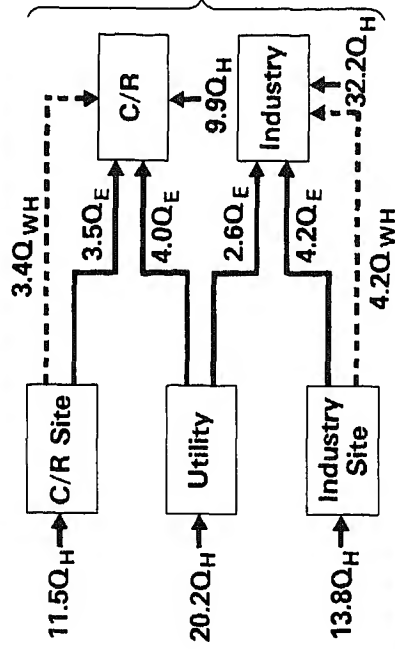
$Q_E$  = Quads Electricity Made/Year

- 33 = Utility Electric Generation Efficiency

- 30 = Cogen Site Electric Generation Efficiency

- 60 = Total Cogen Site Conversion Efficiency

## With Cogeneration

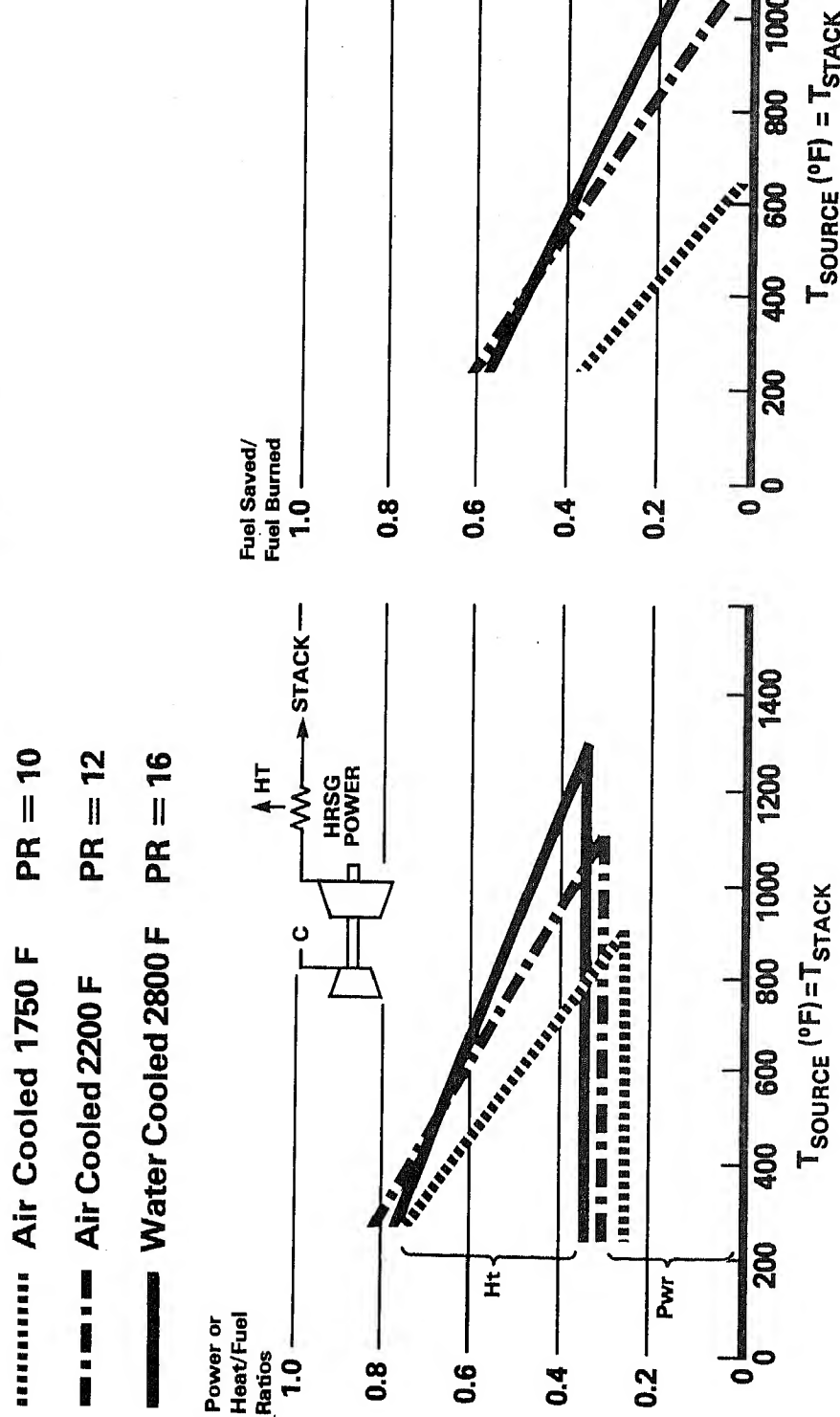


2000

Figure 1

# Gas Turbine - HRSG Cogeneration Characteristics

Figure 2.





this fuel can be substituted which is discussed next.

A very major technical barrier confronting the successful substitution of coal for scarce fuels is the fact the emissions from the combustion of coal derived fuels can be high enough to be considered unhealthy. The two most obvious solutions in engines are to (1) clean up the fuel to remove the pollutants or (2) to develop engine technology to either burn more cleanly or clean up the exhaust products. A third solution, which is not quite so obvious is also applicable in reducing emissions. This third solution is cogeneration - the simultaneous generation of electrical or shaft power and process heat. The technical key to understanding how cogeneration can reduce emissions lies in understanding that in a "topping" type cogeneration system, the waste heat from a powerplant is used to make process heat instead of firing up an isolated furnace. The emission reduction comes from the industrial or commercial/residential furnace that is no longer lit. These 2 sectors now consume about 7 quads of electricity and 34 quads of fuel for heat, mostly in isolated non-cogenerated installations. In the future these requirements may be even greater and come to us at a time when it would be most desirable to meet these requirements using our most abundant fuel - coal. Means to do this job without sacrificing our environment however, are badly needed. Within these constraints it appears that cogeneration can be one of the most promising ways to make the combustion of coal acceptable for both power and process heat generation. The solution which this paper offers, cogeneration, not only reduces emissions it also is highly fuel efficient and can provide a market for the more economic, minimally processed coal-derived fuels. Some of the technical reasons why coal-derived fuels are not being used this way today even on a trial basis, are that (1) the best\* of today's engines for cogeneration (diesels and gas turbines) can have severe operating problems on the impurities in these fuels. (2) even the emission reductions possible through only cogeneration are not enough to meet proposed EPA engine standards and (3) critical technologies for the balance of the coal cogeneration plant beyond the engine have not been investigated enough to know what their problems and solutions are. If these problems can be solved, there is still some barrier potential for industrial or commercial/residential cogeneration that can be anticipated if the environmental standards are based upon emissions per BTU input rather than emissions per usefull BTU output. In a cogeneration system, the usefull output can be on the order of 3 times higher than that of an isolated non-cogenerated powerplant with no increase in site emissions, despite the very large increase in usefull energy conversion. It seems very reasonable to the author that an environmental credit should be given for this added capability in BTU or equivalent KWHR that cogeneration can provide.

The following develops the rationale for these claims of emission reduction and increased useful output. Refer to Figures 2 to 5. Figure 2 from Reference 1 shows a candidate open cycle gas turbine cogeneration scheme making both electricity from a shaft driven generator and low temperature

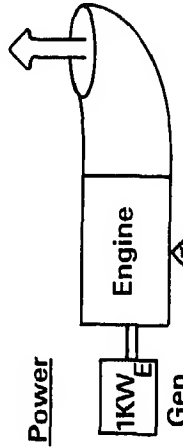
\*1) Best here means highest power/heat ratio.

Figure 3.

# Effect of Cogeneration Upon Emissions

Isolated Power and Process Heat Production  
(No Cogeneration)

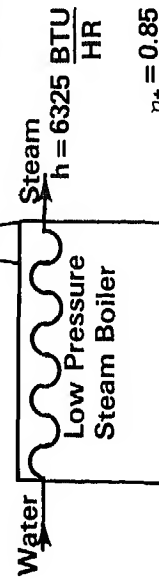
230 PPM NOX  
Exhaust  
(0.7 Lbs/10<sup>6</sup> BTU)  
 $\eta_t = 0.30$



0.7% FBN  
11500 BTU/KWHR

230 PPM NOX  
10<sup>6</sup> BTU  
Exhaust

Process Heat



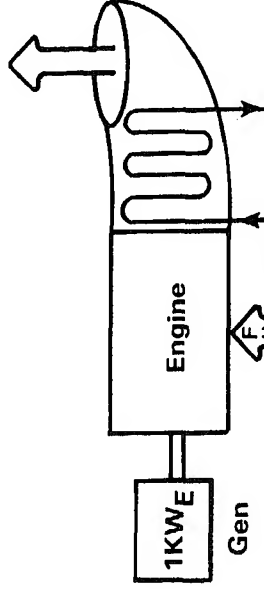
$\eta_t = 0.85$

0.7% FBN  
7441 BTU/HR

$$\boxed{\text{Isolated Lbs NOX/HR}} = \frac{.007527 \text{ Lbs}}{\text{HRE}} + \frac{.002232 \text{ Lbs}}{\text{HRH}} = \boxed{.00976 \frac{\text{Lbs}}{\text{HR}}}$$

Integrated Power and Process Heat Production  
(Cogeneration)

230 PPM NO  
Exhaust



11500 BTU/KWHR

11500 BTU/KWHR

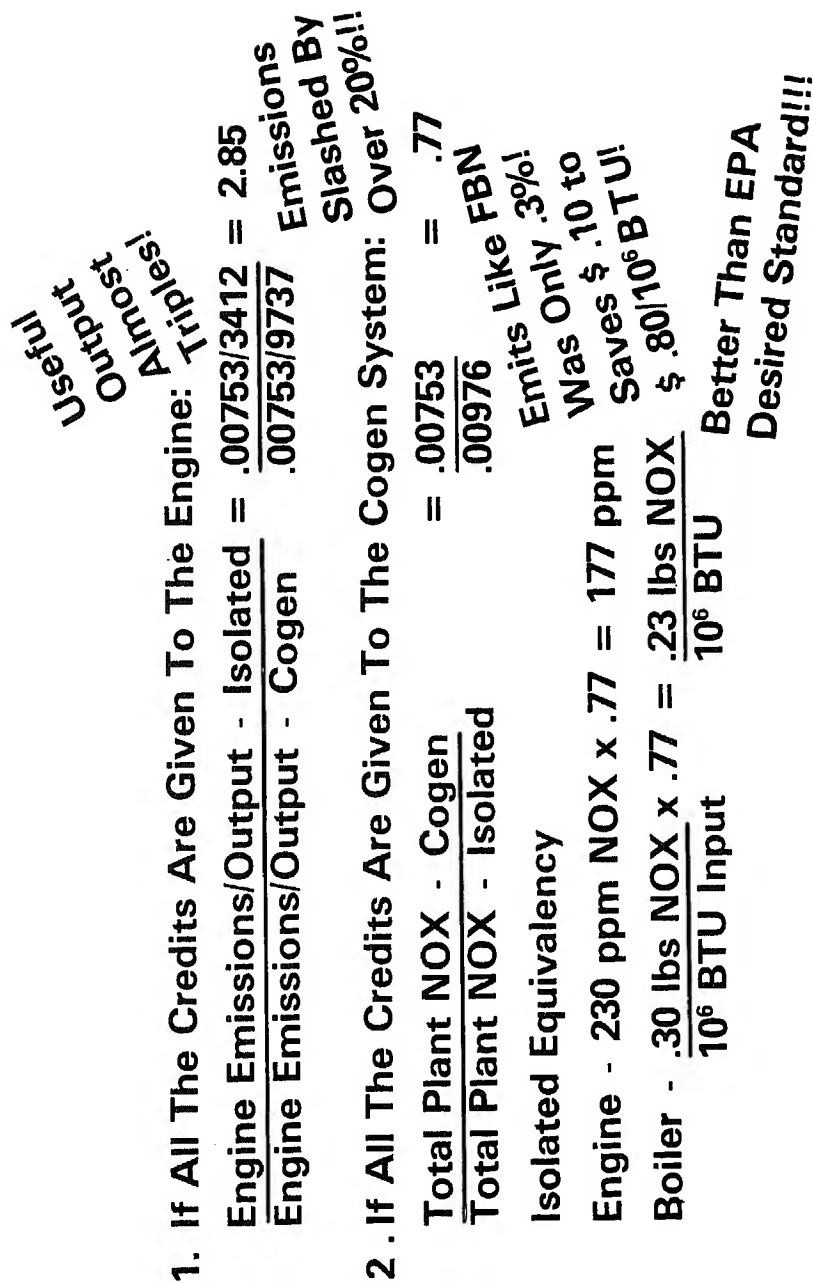
$$\eta_t = .85 = \frac{3412 \text{ BTU}_E + 6325 \text{ BTU}_H}{11500 \text{ BTU}_{\text{Fuel}}} = \frac{9737}{11500}$$

Cogenerated Lbs NOX/HR

$$= .007527$$

Figure 4.

# Taking Credit For Cogeneration Benefits On .7% FBN Coal Liquid



the boiler which does not have to be replaced  
now comes from the cogeneration system.

For a direct comparison of emission and fuel reductions between isolated and cogenerated power and process heat generation on coal-derived fuels, see Figure 3. This figure shows an isolated boiler making low pressure process steam and an isolated gas turbine making electrical power. For illustration and comparison purposes, the boiler is sized to put as many BTU/HR into steam as the cogenerated gas turbine does. To make the case scaleable, the electricity generated is 1 KW. In the illustration, the fuel used is an undefined coal-derived liquid containing .7% fuel bound nitrogen with both the boiler and the turbine using the same fuel. The fuel bound nitrogen level selected corresponds closely to that of fuels that were burned in a gas turbine combustor (Ref. 2) and in a utility furnace that had originally been sized for coal (Ref. 3 and 4). The engine and boiler emissions of NO<sub>x</sub> shown in Figure 3 are therefore, based upon actual coal-derived liquid fuel burns in production equipment. No speculation is made in this paper as to whether or not these values are going to be typical, but the ones shown do reflect what was measured. Cogeneration is shown to reduce the system emissions of NO<sub>x</sub> by 23% owing to the elimination of the boiler, its fuel demand and the emissions from that fuel. This brings up a subtle but very important point, that any impact of cogeneration is due to the equipment it replaces. The boiler shown in the example only emitted .3 lbs NO<sub>x</sub>/10<sup>6</sup> BTU fuel input. If, for whatever reason, that emission had been higher, say .7, as might occur on furnaces originally designed for natural gas or light distillate, then the lbs of NO<sub>x</sub>/Hr would have risen from .00223 to .00521 for the boiler contribution. This would have raised total system emissions of NO<sub>x</sub>/Hr from .00976 to .01274. Eliminating such a high emission boiler through cogeneration would reduce total emissions by 41%. The point is that the impact of cogeneration upon emissions is dependant upon what is being replaced.

Figure 4 shows some various aspects of how these emissions reductions might be credited for the user. Two methods are shown. The first method credits the emission reduction uniformly for all members of the system as a whole -rather than to one component of it. In this form of accreditation, the total NO<sub>x</sub> reduction for power and process heat production is 23%. This means that the site of the cogeneration system is only making 77% of the NO<sub>x</sub> that would be formed by an isolated gas turbine plus an isolated boiler. For the boiler this would be equivalent to an isolated unit emitting only .23 lbs NO<sub>x</sub>/10<sup>6</sup> BTU, which is considerably better than EPA standards. For the gas turbine, a 23% reduction in NO<sub>x</sub> would be equivalent to reducing its

- \*1) Ref. 1 also shows a combined cycle gas turbine (42% efficiency) with its waste steam going directly to process heat with 70% cogeneration system efficiency in the 300° - 400°F stack temperature range.

is worth noting that based upon Ref. 2's information, a reduction in NOX from 230 ppm to 177 ppm is equivalent to operating an isolated engine on .3% FBN fuel rather than .7% FBN. In a system that combined both cogeneration and an advanced low NOX combustor gas turbine, the minimally processed .7% FBN fuel might have been used and the additional fuel cleanup cost avoided. Over a 5 year period, operating 65% of the time (28470 hrs), a fuel cost savings (by being able to use .7% FBN instead of .3% FBN fuel) of \$.60/MBTU (Ref. 5) would result in a savings of \$196.40/KW. Since this figure is higher than the installed price of a gas turbine, it suggests that just the savings in not having to do additional fuel cleanup would pay for the powerplant in 4-5 years.

Compared to the isolated system, the cogeneration system only consumes 60% as much fuel for the same output. One way of interpreting this is that the cogeneration system could possibly more easily afford a substantial increase in fuel price if it were to rise from \$3/MBTU (today's price) up to \$5/MBTU (a possible future price).

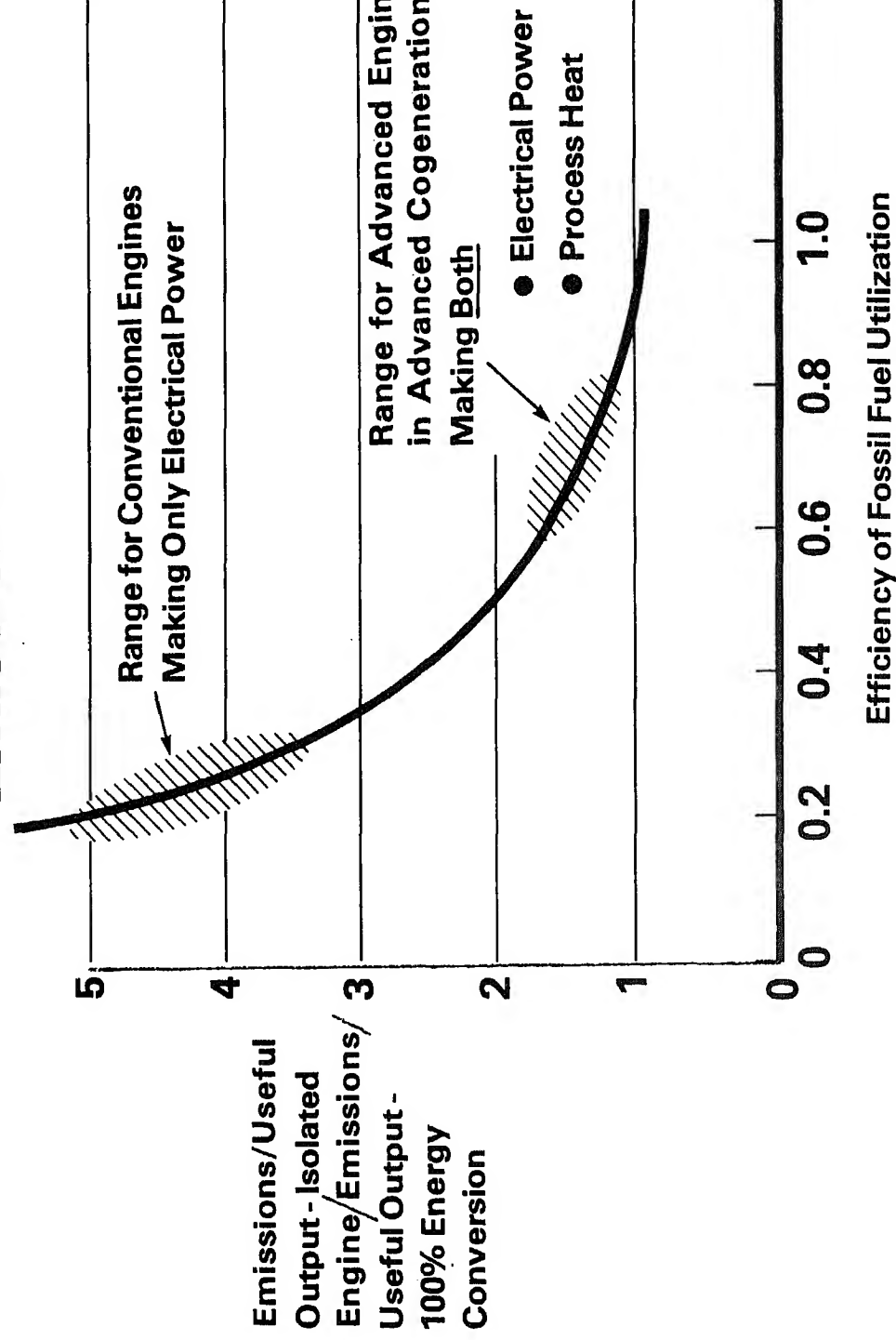
In summary, the substantial impacts of cogeneration for the case given were:

- 1) An actual fuel consumption reduction of 40%, and an attendant NOX reduction of 23 to 41%, depending upon the performance of the replaced boiler.
- 2) An ability to burn minimally processed coal-derived fuels, rather than the more highly processed varieties with a savings over a 4 to 5 year period big enough to pay for the installed capital equipment price of even advanced gas turbine powerplants.
- 3) An ability to tolerate a rise in fuel price from \$3/MBTU up to \$5/MBTU - if the fuel is used in a cogeneration system - with no increase in price of either electricity or process heat to the customer because of a fuel price increase.

The second method gives all the credit to the engine due to the fact that although it's emissions do not change, its output in terms of useful BTU's goes up by a factor of 2.8. This output per emissions factor is simply the ratio of engine thermal efficiency with and without cogeneration. Usually this does not mean that emissions are reduced by a factor of 2.8. There are certain cases however, where it does mean exactly that. These are the cases where heat can be supplied in lieu of electricity for direct element heating, particularly where this electricity comes from peaking gas turbines. For the case given, if the cogenerated low pressure steam (or hot water) could replace electricity made by isolated gas turbines like the one in the example, the NOX produced to make the same useful output (9737 BTU) would be .00753 lbs, rather than  $(9737/3412) \times .00753$  or .0213 lbs, which is lower

# The Impact of Advanced Cogeneration on Emissions

Figure 5.



discussion of their individual behavior in cogeneration systems too lengthy for this paper. However, some gross definition of the impact of cogeneration upon the emissions of the cycles is still desirable. An attempt to show this is given in Figure 5.

Figure 5 shows the ratio of emissions/output for isolated powerplants to emissions/output for 100% energy conversion plotted versus installed thermal efficiency. This curve is a direct presentation of the second method of accreditation given previously in which all the credit for the conversion to additional useful energy is given to the engine. The message from the figure is that cogeneration can boost the useful power and heat output of engines by factors as high as 3. While this does not reduce the site emission level for power generation, it does reduce the need for combustion of a fuel elsewhere to get the extra output now being made through cogeneration. In the example given, the ordinate value for the isolated gas turbine making only electrical power is 3.33 and the value for the cogenerated gas turbine is 1.18. The ratio of those two values is 2.8 which means the output of the cogenerated system is 2.8 times as much as the isolated system with no increase in fuel consumption or emissions.

The preceeding has given a reasonable indication that cogeneration can have a large beneficial effect not only in reducing emissions but also in making large financial savings in the life cycle of power and heat generation on minimally processed coal-derived fuels. Cogeneration seems to be a means of overcoming many of the technical, economic and environmental problems associated with coal. In recognition of such powerful leverage, in FY 1978 and FY 1979, the Fossil Energy Group of Energy Technology at DOE has established a series of major programs intended to (1) identify the major opportunities for cogeneration on coal and (2) to develop the technology in engines to permit them to operate reliably and cleanly on the lower cost minimally processed coal-derived liquid fuels.

In the first area, the 1985-2000 time frame is being addressed with major emphasis on obtaining optimum matches between engines of all types and the electrical and process heat requirements of 6 major industries and a commercial/residential mix. The industrial program now constitutes 2 major parallel study contracts (GE and UTC) let through NASA, Lewis Research Center. They are investigating the technical merits of diesel, stirlings, gas turbines, steam turbines, fuel cells, thermionics, bottoming cycles and energy storage for cogenerating the chemical, refining, paper, metals, stone/clay/glass/cement, and food industries with extensive applications of coal-derived fuels being sought. This program is called the "Cogeneration Technology Alternatives Study" (CTAS) and the contracts end in March 1979. The commercial/residential study is termed "Total Energy Technology Alternatives Study" (TETAS) which is being conducted in-house at Argonne National Laboratory. In this study, ANL is trying to find optimum matches between most of the topping cycles and heat pumps of CTAS and the power/heat requirements of a commercial/residential mix - shopping center, townhouses,

The one major assumption of the above studies is that they, by definition, presuppose that engines can operate at least reliably and possibly cleanly on coal-derived fuels. With the exception of the steam turbine, this is not necessarily true today. Fortunately, however, Fossil Energy in DOE has made major strides in establishing engine programs to provide the fuel flexibility capabilities that the studies assume exists. The major thrust of the programs are in diesels, gas turbines and Stirlings. The Stirling has the most fuel flexibility of all, because like the steam turbine it is externally fired which means its working fluid never comes into contact with the products of combustion. The Stirling's problem is that its major development for widespread commercialization was stopped around the turn of the 20th century due to the availability of cheap, clean, fuels suitable for internal combustion engines. Fossil Energy will have 2 small units built and scheduled for their first run in FY 1979. The conceptual design of a large unit will be started in FY 1979 with the first engine to test about 5 years later. The gas turbine can burn mostly any liquid or gas that is combustible, including coal-derived fuels. The gas turbine's problem on coal-derived fuels is that without additional processing of the fuel, many of these fuels contain traces of what is in coal - namely fuel bound nitrogen which produces high NOX levels, ash which may give turbine erosion problems and minute quantities of vanadium and alkali metals that give the turbine severe corrosion problems. The solutions to these problems seem to be the development of coatings and low-NOX combustor techniques. Two major DOE programs in these two technologies will be on multiple contract by January, 1979. With adequate funding, the programs will last about 5 years each and will be complete with demonstration in an engine(s). This work dovetails with complimentary development efforts on gas turbines for utility companies being performed through EPRI for baseload and intermediate capability on residual oils and coal-derived fuels. Of the three power-plant types mentioned, the one which seems closest today to a multi-fuel capability is the stationary diesel. This is based upon the fact that under DOE sponsorship several coal-derived liquid fuels have been run in a large diesel engine with less than a 10% increase in NOX as compared to light distillate operation. DOE plans to initiate a program in FY 1979 that will more fully assess a range of stationary diesel sizes on coal-derived liquid fuels. The primary things to be learned relate to emissions, corrosion, erosion, deposition, wear and what it takes to get fuels with very low cetane numbers to ignite.

The overall conclusion of this paper is that cogeneration offers a very powerful technique for the successful use of coal as a means of reducing oil imports, emissions, fuel costs and operating costs. The key technologies will require continued development in three major complimentary areas - coal-derived fuel processing, engines to burn these fuels cleanly and reliably and all other critical components needed to cogenerate besides engines and fuels.



Schenectady, NY 12345

2. Efforts performed in 1978 under "Combustors for Coal-Derived Liquids With High Bound Nitrogen," EPRI Contract RP 989-1, by Westinghouse Electric Corp., Lester PA 19113
3. Mr. Richard Corey, DOE/ET/FE, Oct. 1978, 20 Mass. Ave. N.W., Washington, D.C. 20545
4. Mr. Don Teixeira, Oct. 1978, EPRI, 3412 Hillview Avenue, P.O. Box 10412, Palo Alto, CA 94303
5. "Economic Screening Evaluation of Upgrading Coal-Liquids to Turbine Fuels" AF-710, Technical Planning Study 76-666, Final Report March 1978, by Mobil Research and Development Corp., Billings Port Road, Paulsboro NJ 08066, EPRI Project RP 361-2



Chairman: William Peters

Co-Chairman: Fred Witmer



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A high resolution mass spectrometric (HRMS) screening technique developed at the Pittsburgh Energy Technology Center (PETC) was used to screen process streams from coal gasification and liquefaction for possible hazardous compounds. The screening technique compares precise masses determined by high resolution mass spectrometry to those masses of chemical formulas corresponding to selected hazardous and/or toxic compounds. The hazardous compound list employed in the HRMS screening program is comprised of nearly 700 hazardous compounds from OSHA, EPA, NIOSH, ACGIH, and NAS lists. HRMS screening data was obtained on coal gasification tars and all the major process streams from the PETC 400 lb/day liquefaction PDU. Liquefaction product made with an added catalyst was found to contain fewer possible hazardous compounds than product made without added catalyst as determined by the HRMS screening technique. Concentrations of specific compounds in process waters from both gasification and liquefaction processes were determined by direct injection gas chromatography.

METHODOLOGY DEVELOPMENT FOR THE DETERMINATION OF POLYCYCLIC  
AROMATIC HYDROCARBONS (PAH) IN FUGITIVE EMISSIONS  
FROM COAL LIQUEFACTION PROCESSES

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The objective of this project is to develop a method for the quantitative collection and analysis of polycyclic aromatic hydrocarbons (PAH) in fugitive emissions from coal liquefaction processes. Coal liquefaction products and

Toward this objective, it has been shown that PAH can be quantitatively recovered from ambient air, and the collected sample can be quantitatively recovered from the collection media by solvent extraction, using n-pentane. Further, dilute solutions of PAH in n-pentane can be concentrated by solvent removal using a Kuderna-Danish evaporative concentrator, with minimal sample losses. The chromatographic resolution of complex mixtures of PAH expected to be present in fugitive emissions from coal liquefaction processes is best attained using high resolution glass capillary-gas chromatography. The gas chromatographic retention characteristics of over 200 PAH have been determined, and a new gas chromatographic retention index system unique for PAH has been developed. The PAH retention index system provides for the tentative identification of numerous PAH in these complex mixtures. Positive identification is obtained when the retention indices are combined with mass spectral data on the same chromatographic peaks. The use of the new PAH retention index system will be demonstrated by the analysis of an aromatic fraction from a coal liquefaction product.

## INTEGRATED COMPLIANCE AND CONTROL TECHNOLOGY RESEARCH ACTIVITIES FOR IN SITU FOSSIL FUEL PROCESSING EXPERIMENTS

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U.S. Department of Energy  
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Fossil fuel processing research facilities must comply with Federal and state regulatory standards. In addition, the experimental sites provide research opportunities to evaluate control needs and then design and demonstrate control measures as each technology approaches commercialization. This paper will summarize the regulatory compliance and control technology activities and illustrate their integration as pertaining to field in situ recovery experiments for oil shale.

Wastewater disposal is an important element to be considered in evaluating the environmental impact of the developing shale oil industry. Wastewater can be generated by a number of different sources within a shale oil recovery facility, depending on the type of recovery system used, the location, and the type of oil shale processed. The pollution potential of the wastewater may be very high as in the case of retort water or it may be low as in the case of some minewaters. Above-ground retorts may reuse all wastewater streams generated within the mining and processing facilities to moisten spent shale for compacting in the dumping areas. Moisturizing spent shale is not performed at in situ operations; therefore, substantial wastewater discharges are anticipated at their installations. In situ retorting produces water in approximately the same volume as the oil produced, consequently a 100,000 barrel per day facility would generate about 4 million gallons of retort water each day for disposal.

Studies have been completed on the evaluation of land disposal and underground injection as disposal options for shale oil wastewaters. Land disposal is the application of wastewater at the soil/air interface to utilize natural chemical and physical reactions for purifying the wastewater. Underground injection makes use of deep confined aquifers or isolated geological zones for discharge of wastewaters. The results of this investigation indicate that both the wastewater characteristics and the climate of the oil shale regions of Colorado, Utah, and Wyoming are not favorable for land disposal of retort water. Underground injection is a viable disposal option for retort water where geological conditions are favorable; however, regulatory restraints are expected to limit the use of this option.

Studies are currently in progress on benchscale evaluations of treatment technology for retort water and mine water. Conventional biological treatment appears to be adversely affected by toxicants in the retort water, however, preliminary results indicate that the addition of powdered activated carbon may overcome this problem. Several different methods have been investigated for removal of fluoride, boron, and alkalinity from minewaters. Ion exchange is a leading candidate for treatment of minewaters.

Burned out oil shale retorts need to be stabilized to prevent subsidence of the overburden and the ground surface; prevent gas leakage; maximize resource utilization; and provide subsurface disposal of spent shale that has been retorted on the surface and minimize ground water contamination.

We believe that in order to stabilize the retorts, the following strategy should be followed.

- (1) Characterize the components of the retort such as overburden and pillar strength: temperature effect on strength; retort and pillar permeability; and rubble behavior during and after retorting.
- (2) Develop slurry that can accommodate a maximum amount of spent shale and low quality water.
- (3) Investigate techniques for emplacing the grout and sealing the retorts.
- (4) Develop a retort cooling process whereby sensible heat can be recovered and the residual rubble will have properties amenable to grouting.
- (5) Prepare a full scale field test program to evaluate the optimum combination of cooling procedures, grout and emplacement techniques.



The injection of wastes into deep underground formations is the most economical method for disposal of liquid wastes that are not amenable to surface treatment. Operating costs are lower for pretreatment and subsurface disposal than for surface treatment systems, and plant area requirements are less. Chemical treatment is minimal, and generally the only physical treatment required for underground injection is filtration. This report presents a broad view of modern industrial underground waste injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

The petroleum industry has been injecting fluids into subsurface formations for many years; therefore, many of the techniques and much of the equipment for handling industrial liquid wastes are already available for industrial waste disposal or can be modified to meet the specialized requirements. The techniques for drilling and completing the disposal wells have been perfected, and the equipment to do it is in service. Similarly, the behavior of fluid flow through porous rocks and unconsolidated sand has been investigated; therefore, many of the theories and equations describing the fluid distributions have been proved. Modification may, however, be needed to make them applicable to waste injection systems and to describe the radial chromatographic properties of the injected wastes constituents.

A subsurface disposal system can be successful only if a porous, permeable, formation of wide areal extent is available at sufficient depth to ensure safety in storage and retention of the injected fluids. The wastes usually are treated for solids removal and compatibility with the formation. An impermeable zone, such as shale or evaporite, must overlie the injection horizon to prevent vertical migration of the waste or displaced formation brines into low-salinity aquifers above the disposal zone.

General principles of design and construction are applicable to all subsurface injection systems; therefore, this report is presented in three parts. First the general technology of subsurface disposal systems is presented with notations on cost; second, the general geology of the United States is discussed with reference to subsurface waste disposal; and third, detailed discussions are presented on disposal systems that illustrate particular design and operating features.

Paper not submitted for publication in Proceedings.

SCREENING COAL GASIFICATION AND LIQUEFACTION PROCESS  
STREAMS FOR POSSIBLE HAZARDOUS COMPOUNDS

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Paper not submitted for publication in Proceedings.

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Paper not submitted for publication in Proceedings.

## ABSTRACT

Fossil fuel processing research facilities must comply with federal and state regulatory standards. This paper summarizes the research effort in effect at the Laramie Energy Technology Center and regulatory requirements pertaining to control technology for process waters associated with in situ oil shale processing. In addition, the experimental sites provide control needs and then design and demonstrate control measures as each technology approaches commercialization.

## INTRODUCTION

The Laramie Energy Technology Center (LETC) is primarily responsible for the development of in situ recovery technologies related to such alternate fossil fuel resources as oil shale, coal, and tar sands. Advancing in situ technologies to commercial practicability involves a progression of field experiments through which the engineering, environmental, and economic issues can be explored and resolved. In 1977, legislation was passed requiring federal facilities to comply with federal, state, and local regulations and standards when conducting field experiments. Environmental efforts at LETC address compliance requirements at field sites and generate information that can be transferred to industry and environmental regulatory agencies as in situ technologies approach commercialization. This paper will illustrate, through specific examples, the development of control technology in conjunction with compliance requirements.

## BACKGROUND

The goals of the environmental effort at LETC are (1) to identify, quantify, assess, and reduce to within acceptable levels any adverse environmental impact that may result from in situ fossil fuel processing field experiments conducted by LETC and (2) to accelerate the acquisition and application of environmental and compliance data related to in situ fossil fuel processing so as to move the technologies towards commercialization.

The development of in situ processing technology is primarily accomplished through a schedule of field experiments. Environmental research

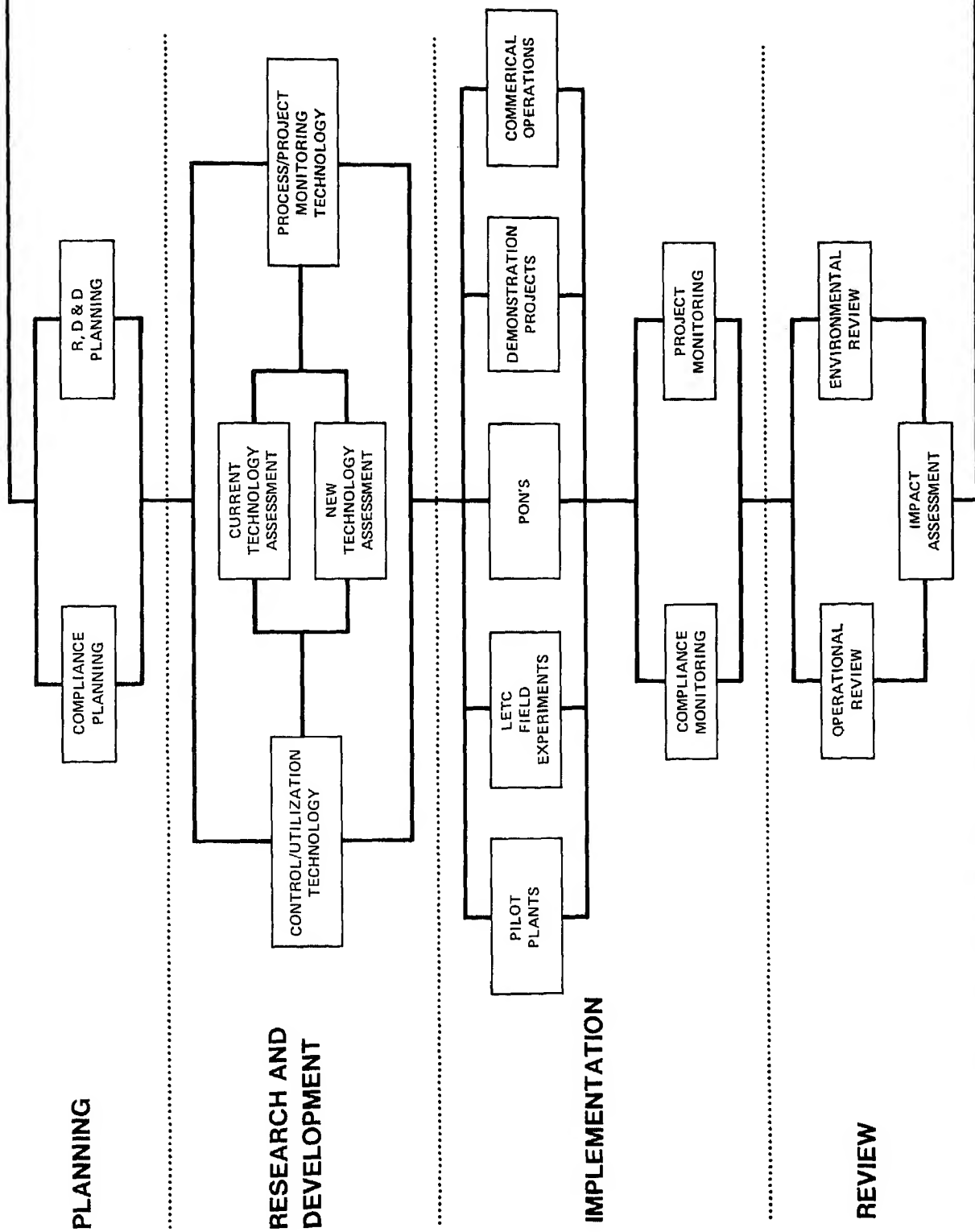


FIGURE 1. LETC ENVIRONMENTAL ACTIVITIES

coordinated and integrated use of every field experiment to further both process and environmental RD&D efforts. In many instances, environmental work is conducted outside of the field activity (e.g., laboratory, review, or assessment work). Nevertheless, under the LETC approach such work is either derived from or oriented towards a field activity.

The general approach for the environmental activity at LETC is shown in Figure 1. This diagram illustrates the primary areas (in boxes) associated with various stages of environmental activity as it progresses from planning, through R&D, to implementation, and review. These stages are iterated to account for the changing implementation focus as it progresses from pilot plant facilities to commercial operations. Within this framework, all subjects of environmental concern are addressed, including potential air, water, land, ecologic, socioeconomic, occupational, and aesthetic impacts.

It should be evident from Figure 1 that the scope of environmental work at LETC is quite broad. LETC in house field activities are also numerous, with projects currently in progress near Bonanza, Utah and Rock Springs, Wyoming (oil shale), Hanna, Wyoming (underground coal gasification), and Vernal, Utah (tar sands). To more effectively illustrate the inter-relationship of compliance activities related to field projects with other environmental efforts, specific subjects have been selected; namely, the Rock Springs experimental in situ oil shale facility and control technology for in situ oil shale process waters. Water-related problems are pertinent to all in situ technologies from both regulatory and research points of view. Thus, this discussion will address a significant subject in some detail, while at the same time it will serve to illustrate the LETC approach of coordinating and integrating process and environmental research at the field level for all technologies. A summary of environmental research conducted by LETC for in situ oil shale processing, which includes reference to process data, has recently been published (1).

## DISCUSSION OF CONTROL TECHNOLOGY FOR PROCESS WATERS

In this paper the term "process water" refers to all contaminated waters originating in conjunction with the in situ oil shale process. Process waters are derived from the following primary sources: (a) water formed as a byproduct of the combustion of organic matter in oil shale, (b) water released by dehydration of oil shale minerals, and (c) native groundwater associated with or intruding into the retorting zone (1). As a result of their intimate association with the retorting process, these waters become heavily laden with both organic and inorganic constituents. A summary of water quality parameters for process waters derived from both simulated and true in situ retorts is presented in Table 1 (2). This table indicates that process waters characteristically are alkaline and contain high levels of solids and dissolved organics. Principal inorganic constituents include ammonia, ammonium, bicarbonate, carbonate, magnesium, sodium, and various sulfur species. The organic constituents are primarily polar in nature, with carboxylic acids

Parameter	Range		Average	Best Value <sup>c</sup>
Alkalinity, total (mg/l CaCO <sub>3</sub> )	18,200	110,900		16,200 ± 480
Aluminum	0.041	16.6		<0.03 - 19.1
Arsenic	0.46	10	1.8	1.0 ± 0.2
Barium	0.002	0.47	0.07	0.71 ± 0.33
Beryllium	<0.001	<0.001		<0.006
Bicarbonate, mg/l HCO <sub>3</sub> <sup>-</sup>	4,200	73,640		15,940
Biochemical oxygen demand, 5-day	350	5,500		740
Bromine	<0.001	1.94	0.082	2.4 ± .4
Cadmium	<0.001	0.005		0.0016 ± 0.0008
Calcium	0.0	94	7.6	12 ± 4
Carbon, inorganic, mg-C/l	1960	19,200	7,500	3340 ± 390
Carbon, organic, mg-C/l	2,200	19,000	4,700	1003 ± 192
Carbonate, mg-CO <sub>3</sub> <sup>2-</sup> /l	0.0	15,210		500
Chemical oxygen demand	8,500	43,000	18,500	8100 ± 5700
Chlorine	0.007	1910		824 ± 61
Chromium	0.009	0.08	0.015	0.02 ± 4%
Cobalt	0.002	0.65	0.12	0.030 ± 0.012
Conductivity, μmhos/cm	15,100	193,000	31,000	20,400 ± 3840
Copper	0.003	180	0.019	0.10 ± 0.04
Fluoride	0.1	270		60 ± 9
Hardness	20	1,500	88	110
Iodine	<0.001	1.3		0.59 ± 0.30
Iron	0.091	77	7.6	1.2 ± 0.3
Lead	0.002	0.83		0.0045 ± 0.02
Lithium	<0.001	7.1	0.70	0.18 ± 0.8
Magnesium	3.2	350	22	20 ± 6
Manganese	0.001	0.39	0.099	0.09 ± 0.04
Mercury	<0.001	0.39		0.0003 ± 0.021
Molybdenum	0.033	1.2		0.60 ± 0.07
Nickel	0.014	2.6		0.06 ± 0.02
Nitrogen, ammonia, mg-NH <sub>3</sub> -N/l	1,700	13,200	7,000	3795 ± 390
Nitrogen, ammonium, mg-NH <sub>4</sub> <sup>+</sup> -N/l	930	24,450	10,000	3470 ± 830
Nitrogen, nitrate, mg-NO <sub>3</sub> <sup>-</sup> -N/l	1.4	8.7		0.17
Nitrogen, organic, mg-N/l	73.3	1510		148 ± 630
Nitrogen, Kjeldahl, mg-N/l	6,600	19,500		3420 ± 420
Oil and grease	3,800	3,800		580
pH	8.1	9.4	8.7	8.65 ± 0.26
Phenols	2.2	169		60 ± 30
Phosphorus	0.23	19.0	1.25	3.2 ± 2.6
Potassium	8	120	37	47 ± 9
Selenium	<0.001	1.7		0.21 ± 0.11
Silver	<0.001	0.23		0.003 ± 0.001
Sodium	45	1600	320	4333 ± 244
Solids, dissolved	1,750	24,500	6,800	14,210 ± 193
Solids, total	6,350	121,000		14,210 ± 120
Solids, volatile	2,070	119,300		
Sulfur, sulfate, mg-SO <sub>4</sub> <sup>2-</sup> /l	42	2,200	1,400	1990 ± 250
Sulfur, sulfide, mg-S <sup>2-</sup> /l	0.0	156		0.0
Sulfur, total, mg-S/l	14	2320		2300
Uranium	0.018	93		0.55 ± 0.07
Vanadium	0.004	>190	0.27	0.12 ± 0.01
Zinc	0.020	15.1	0.28	0.31 ± 0.04

<sup>a</sup> Selected values taken from reference (2). This reference should be referred to for discussions pertinent to each value given above.

<sup>b</sup> The range given is based on the analysis of up to 18 different waters obtained from 4 simulated in situ oil shale retorts. An average value is given only if 15 or more waters were available.

<sup>c</sup> Best values determined by a statistical technique in the analysis of results obtained from a multilaboratory, multimethod survey of the Omega-9 sample.

field in situ experiments.

The quantity of process waters produced during in situ oil shale processing is dependent upon several factors, including the mineral content of the oil shale, the volume of groundwater present or seeping into the retorting zone, the duration and areal extent of the burn, the amount of organic resource combusted during retorting, and the amount of injected water (1). The ratio of process water to oil produced at the surface during field experiments has been noted to vary from 0.4 to 22.2 (1). The minimum volume of surface-produced process water derived from in situ processing is estimated to be near the volume of oil produced (1). This minimum volume would amount to nearly 5,000 acre-feet of process water per year for every 100,000 barrels of shale oil produced per day.

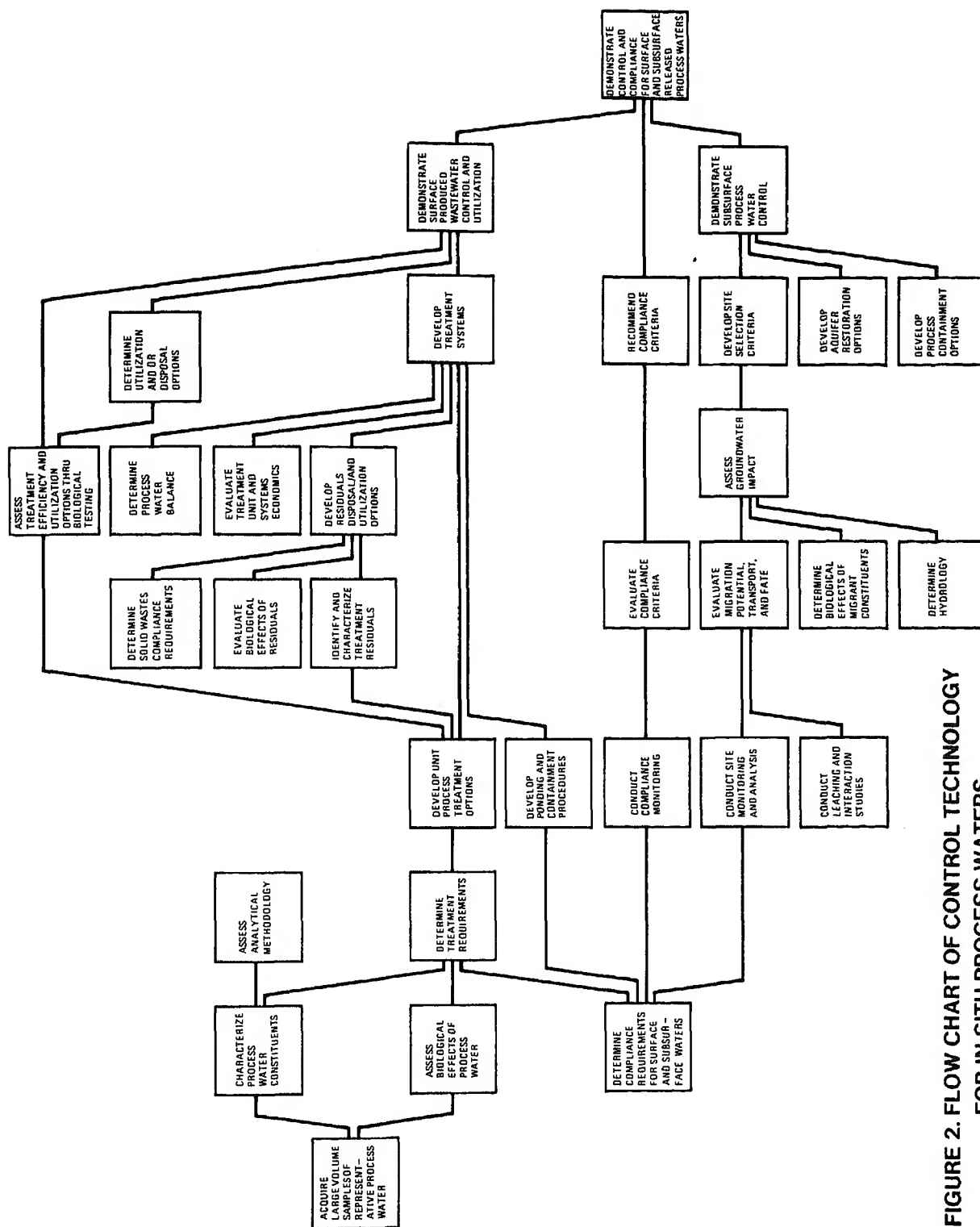
The preceding discussion establishes that low quality process waters originating from the in situ process will have both a surface and a subsurface disposition, both of which pose potentials for environmental contact. The intrusion of groundwaters into retorted zones and their subsequent contamination is another source of possible subsurface disturbance. The goal of process water-related control technology research at LETC is to demonstrate, in conjunction with all applicable compliance criteria, techniques for the effective control and, where practical, utilization of both surface- and subsurface-released aqueous effluents so as to mitigate any undesirable environmental effects. The achievement of this goal is prerequisite to the establishment of a full-scale, commercial in situ oil shale processing industry. Figure 2 illustrates the steps required and the approach being followed by LETC to achieve the goal of control technology for in situ process waters. This figure is largely self-explanatory, and the remainder of this section will be devoted to a discussion of some of the concepts illustrated.<sup>1</sup>

It should first be noted that two primary efforts are being conducted simultaneously; namely, the control of process waters associated with surface and subsurface release. Although not diagrammatically illustrated in Figure 2, many of the work elements provide data and results common to both pursuits (e.g., site monitoring, process water balance determinations, and possible utilization of surface produced waters for subsurface applications, such as steam injection). The determination of appropriate or necessary control, treatment, or utilization options for water released at either the surface or in the subsurface logically precedes systems engineering design efforts. In this program, such a determination is based on two primary inputs. The first input is obtained from examining current or anticipated compliance requirements related to released process waters. The initiating role that compliance

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<sup>1</sup> Reference (1) provides key references to work published up to 1978 in the subject areas indicated. Subsequent citations or additional technical information may be obtained from the authors.





**FIGURE 2. FLOW CHART OF CONTROL TECHNOLOGY FOR IN SITU PROCESS WATERS**

current regulations certainly serve as a basis for design, there is scope for progressive improvement and refinement of these regulations as our knowledge of process water impacts and mitigation options increases.

The second primary input in determining control requirements and options is based on findings and recommendations from research specifically designed to identify impacts resulting from released process waters. Characterization of the constituents in process waters, assessment of the biological effects of process waters, and determination of the migration potential, transport, and fate of process water constituents through site monitoring and laboratory experiments all represent this type of research.

Considering the ever increasing demands on the limited water resources of the semi-arid oil shale-bearing regions of the West, water produced during in situ processing in itself should be considered as a potentially valuable commodity. The possible use of process waters for both on- and off-site purposes is therefore given considerable attention early in the development of unit and process train treatment systems. At this time the most probable uses for excess process waters are related to steam reinjection, site steam generation, heat exchanger and cooling water, and land applications, such as for irrigation during revegetation and rehabilitation of sites. Economic considerations should include consideration of solute recovery from the process waters during treatment as a means of offsetting treatment costs.

An inevitable consequence of any treatment procedure is that a concentration of residuals will be removed from the influent stream. The development of acceptable options for the disposal and/or use of such residuals is considered to be a fundamental part of the overall development of an acceptable treatment system. The multiplicity of potential uses and the rather unique compositional characteristics of process waters considerably limit the applicability of existing water treatment technologies to process water treatment needs. It is therefore necessary that a variety of treatment methodologies -- spanning primary, secondary, and tertiary treatment by physical, chemical, and biological means -- must be explored simultaneously to determine their capability for handling these type waters. There is currently a broad effort under way in this area (1). In the meantime, field experiments will continue to produce excess effluents. A temporary measure available now is to contain such waters until functioning treatment systems are in place. Also, evaporation ponds established at field sites offer excellent opportunities to study ponding practices.

An assessment of the impact that subsurface released process waters and leachates from retorted zones may have on groundwater quality is an active research objective at field sites. Should groundwater quality changes be determined as profound and persistent, then the obvious mitigation procedure would be to select in situ processing sites where the hydrologic, stratigraphic, or other considerations would be such that groundwater disturbance or degradation would be prevented. However, this recourse would limit the amount of available resource. It is therefore necessary that other options for mitigating groundwater impacts be explored. Methods for the containment

The starting point, and the final proving ground, for process water control technology development is in the field environment. It is here that relevant water samples, containing all the variances imposed by the process, are obtained. It is in this environment that the dynamic factors (migration, bioavailability, ecological effects, utilization options) are at work. Thus, it is at these locations where the control technology must first be demonstrated.

## DISCUSSION OF WATER-RELATED COMPLIANCE REQUIREMENTS

Now that some important dimensions of process water control technology have been discussed, it is necessary to examine the legal and regulatory structure within which such processes must function. This section will examine both Federal and Wyoming environmental laws and regulations that impinge upon the implementation of in situ processing technologies involving both surface and subsurface water.

Laws and regulations apply to air pollution, water pollution, land reclamation, toxic substances, solid waste, occupational safety, health, and many other aspects of in situ processing. As noted earlier, we will address environmental regulations as they apply to surface and subsurface water.

### Surface Waters

The Federal Water Pollution Control Act (FWPCA) (3) established goals to eliminate discharge of pollutants into navigable waters by 1985 (4); to achieve interim goals of water quality which provides for the protection and propagation of fish, shellfish, and wildlife (5); and to prohibit discharge of toxic pollutants (6). In order to achieve these goals, industrial facilities can be regulated through three different mechanisms -- standards are established for maintenance of the quality of receiving waters; standards of performance can be established for specific classes of emission sources; and standards can be established for specific toxic pollutants.

### Standards Based on Quality of Receiving Water

The FWPCA bases effluent limitations on water quality of the receiving water:

Whenever . . . discharges of pollutants from a point source or group of point sources . . . would interfere with the attainment or maintenance of that water quality in a specific portion of the navigable waters which shall assure protection and propagation of a balanced population of shellfish, fish, and wildlife, and allow recreational activities in and on the water, effluent limitations (including alternative effluent control strategies) for such point source or sources shall be established which can reasonably be expected to contribute to the attainment or maintenance of such water quality (7).

## Standards of Performance for New Effluent or Emission Sources.

In addition to effluent regulations based upon the quality of receiving waters, the FWPCA orders EPA to establish "National Standards of Performance" for new effluent or emission sources in 27 different industries. "Standards of Performance" are defined as:

...a standard for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator of EPA determines to be achievable through the application of the best available demonstrated control technology, process, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants (8).

In establishing standards of performance, the EPA administrator will take into account the cost of achieving effluent reduction, non-water quality environmental impact, and energy requirements (9).

After standards of performance are promulgated, it will be unlawful for any owner or operator of any new effluent or emission source to operate the new source in violation of any standard of performance applicable to such source (10). Regulations are now in existence for more than 40 different industries. Oil shale, of course, is not specifically regulated at this time.

### Standards for Toxic Pollutants.

The FWPCA also mandates that the EPA administrator must maintain a list of toxic pollutants (11). Each toxic pollutant listed is subject to effluent limitations resulting from the application of the best available technology economically achievable for the applicable category or class of point sources (12). Criteria for best available technology economically achievable shall include characteristics of pollutants (chemical, physical, and biological), amounts, and the degree of effluent reduction attainable through the application of the best control measures and practices achievable, including treatment techniques, process and procedure innovations, and operating methods.

Section 307.(7) of the FWPCA also states, "Prior to publishing any regulations (establishing best available technology economically achievable), the EPA should consult with appropriate advisory committees, states, independent experts, and federal departments and agencies." Emerging technologies such as in situ oil shale processing should be prepared to make informed input to EPA.

If discharges meet the criteria established for (a) receiving waters, (b) best available control technology economically achievable for the applicable industry or (c) toxic pollutants, the EPA or state regulatory agency to which the authority has been granted may issue a permit for the discharge of any pollutant. The permit is a National Pollution Discharge Elimination System (NPDES) permit (13).

A regulation is also in present form for allowing discharge based upon the water quality of the receiving water. While performance standards are subject to research, existing field facilities must comply with regulations designed to protect the quality of the receiving body of water.

Each state was given the opportunity to adopt water quality standards for the water of its state. Wyoming defines its water to include both surface and subsurface waters. The EPA has approved Wyoming's surface water quality standards and allows Wyoming to enforce the National Pollution Discharge Elimination System's permit system. In addition to surface water quality standards, standards for pollution of groundwaters are being proposed in Wyoming.

In Wyoming the law prohibits any person, except when authorized by a permit, to alter the physical, chemical, radiological, biological, or bacteriological properties of any waters (14). The Wyoming act also forbids construction of any facility capable of causing or contributing to pollution. While standards of performance do not exist for the oil shale industry, LETC research facilities must comply with regulations based upon water quality for receiving waters. Hence, extensive data must be obtained for compliance purposes.

### Subsurface Waters

Regulation of subsurface water pollution is rapidly developing. Wyoming recently proposed water quality criteria for seven classes of water. Contamination of subsurface water will then fall under their permitting system. Wyoming intends to maintain the physical, chemical, radiological, biological, and bacteriological properties of its subsurface waters. Consequently, in situ industries must be able to prevent contamination or restore water to its original condition.

Regulations promulgated under the Safe Drinking Water Act (15) will require State underground injection control (UIC) programs to prevent underground injection which endangers drinking water sources (16). Critical to the in situ oil shale industry will be definitions of "underground drinking water sources" and "underground injection."

The Act defined underground injection as the subsurface placement of fluids by well injection (17). Proposed definitions (18) defined well injection as "subsurface emplacement through a bored, drilled, or driven well." The proposal also defined an underground drinking water source as "any underground source with a level of total dissolved solids of 10,000 mg/l or less" (19).

The "regulations may not interfere with or impede (a) the underground injection of brine or other fluids which are brought to the surface in connection with oil or natural gas production, or (b) any underground injection for the secondary or tertiary recovery of oil or natural gas, unless such requirements are essential to assure that underground sources of drinking water will not be endangered by such injection" (20).

program may designate one or more aquifers or portions thereof in the state which have a total dissolved solids level below 10,000 mg/l which will not be protected because they are oil producing, are severely contaminated or located in such a way that use as drinking water is impracticable" (21).

Subsurface water quality standards will be extremely important to in situ oil shale development. The selection of in situ processing sites so that they do not interfere with subsurface waters or the development of restoration methods for such waters to their original quality are important considerations for control technology.

#### EXAMPLE PROJECTS INTEGRAL TO COMPLIANCE AND CONTROL

The previous discussion points out that there are federal and state regulations on water quality standards for both surface- and subsurface-produced aqueous effluents to which a potential in situ oil shale processing industry must adhere. Also field experiments must comply with all applicable regulations and meet established criteria for water control. In the absence of rigorously defined techniques and systems to control and simultaneously utilize produced waters, field experiments must employ certain expedencies which are acceptable under the law. An example of this is the use of containment and evaporation ponds constructed in accordance with state regulations and guidelines. While limited at this time in terms of employing sophisticated control technology capabilities at field sites, such sites do nevertheless offer prime opportunities for developing and demonstrating such capabilities. Despite of current limitations in applied control technology, field experiments can be conducted so as to meet applicable compliance criteria. The use of an evaporation pond serves to illustrate this point.

An evaporation pond will be used for disposal of process waters during operations at Rock Springs Site 12 (scheduled for operation in November 1978). This pond was designed to contain 100,000 gallons of water, was constructed in accordance with Wyoming Division of Environmental Quality (DEQ) guidelines for wastewater ponds, and required a permit from that agency. With respect to monitoring, the state requires that a leak detection system be incorporated as a design feature of the pond. However, research activities which will be associated with this pond also will include monitoring and analysis of volatile emissions, measuring evaporation characteristics, analysis of surface layer materials, analysis of dissolved solutes and changes resulting from weathering and biological activity determination of the amount and content of residues, and monitoring solar radiation, wind speed, wind direction, and ambient temperature. In addition, studies of pond liner compatibility with process waters and shale oil were performed prior to the selection of the liner used in the pond. These studies exceed those required by the state, but utilize the opportunity afforded by the pond to better define pond characteristics. The additional data to be obtained from the Rock Springs Site 12 evaporation pond will provide the first characterization of physical and chemical aspects associated with ponding of process waters. These data

as a sedimentation step), these additional data will augment our knowledge of control procedures and options.

Discussion of the environmental research related to acquiring an in situ mining permit from the Wyoming DEQ for operation of Rock Springs Site 12 will serve as another example of projects integral to both compliance with regulations and development of water control technology. The in situ mining permit requires evidence of specific plans to restore any disturbed aquifer so that the water quality is equal to or better than it was prior to the activity. Figure 2 illustrates that, with respect to subsurface process waters, the ultimate objective is to demonstrate appropriate control so that no adverse environmental impact will occur. Three control approaches for achieving this are shown in the figure -- site selection, aquifer restoration, and process containment. The current plan leading to aquifer restoration will be discussed after a few remarks pertaining to the other two approaches.

The first approach is related to site selection criteria. The development of site selection criteria means that one must determine what type and to what degree subsurface environmental data are required in order to locate an in situ process where no groundwater impacts will occur even if ancillary subsurface control features are not used. It is possible that appropriate site selection would not require additional control of subsurface process waters if it could be established that there would be no contact between these waters and native groundwaters. Detailed hydrologic and geologic data may be required to determine such a finding. Specifically what data is required to allow for such site selection (including compliance data) is the focus of this approach.

The second approach, development of containment options, entails defining ways of lessening any intermingling of subsurface process waters with resident groundwaters. Diversion of aquifers up-dip of retort zones might be one option to be considered in this approach.

In the third approach, aquifer restoration, the present plan involves three interacting areas of activity. These are: site monitoring; solute leaching, transport, and interaction research; and field restoration trials. Each of these three activities will be discussed in turn. Site monitoring activities pertain to pre-operational, operational, and post-operational monitoring and analysis of subsurface waters located within, peripheral to, and at some distance from fracturing and in situ retorting experiments. Significant examples of this activity can be found in conjunction with Rock Springs Sites 4, 6, 9, and the current Site 12 operation (1). Post-operational monitoring of Site 4 has been in progress since this site was retorted in 1969. Monitoring of backflood waters, a subject significant to the leaching of spent retorts, is a part of each of these site activities. The water monitoring program being conducted in conjunction with Site 12 was developed using knowledge gained in prior experiments and will serve as a focal point for overall assessment of subsurface migration phenomena resulting from in situ experiments conducted in the Rock Springs area. In order to facilitate this task, all relevant water quality data are assembled in a computer system

At the same time, several studies are in progress dealing with the physical and chemical interactions associated with subsurface-produced water release and migration. Such studies include examinations of the leaching of retorted shale, the interaction of process waters with consolidated subsurface soils, sediments, and aquifer materials, and solute transformations in waters remaining or migrating from the retort zone. These studies are primarily oriented towards defining the mechanisms underlying phenomena observed during monitoring. This knowledge also will aid in the extrapolation of trends witnessed during monitoring activities to predict the ultimate probable fate and disposition of subsurface waters associated with in situ processing.

The third activity essential to the aquifer restoration plan involves field trials at the Rock Springs area. The previously described activities will serve to quantify and model aquifer disturbances. This field activity will explore and test methods for correcting any such disturbances. A preliminary step is the evaluation and selection of procedures. Two options are currently under consideration. One is to seal the retorted zone to prevent future contact between groundwaters and spent shale, and thus eliminate possible contamination through leaching. A project has been initiated in this regard which will select and test possible sealing agents (grout, cement, polymers, etc.) (22). One limitation of this option is that it does not address the question of process waters which may have been released during the course of retorting. Another option is to recover the process/groundwater emanating from the retort area and to treat such water at the surface to a degree suitable for reinjection into the retort zone. There is currently some evidence to suggest that a few cycles of this type would be sufficient to remove leachable materials from the retorted shale surface (22). This option would appear to be economically more attractive than the first option, especially since it uses treatment facilities which will be in place to treat surface-produced waters and because it may be relatively easy to equal or improve the quality of groundwaters (particularly at Rock Springs) through a treatment scheme.

As soon as sufficient data are available to decide which of the two options discussed is the more attractive, current plans call for testing the techniques at selected field sites. Use of the Rock Springs sites will take maximum advantage of the extensive site-specific data previously gathered during earlier activities (e.g., monitoring, transport and interaction research, and backflood water analysis). The efficacy of the option being tested could be determined largely through the use of existing monitoring wells. Following evaluation of the first field trial, a second, and more exacting, control experiment is planned. The second experiment is to be executed during 1981 at Site 12. An accelerated effort will be needed to achieve these field experiments. The goal is to demonstrate the selected aquifer restoration technique at Site 12 which will serve to advance our capabilities of subsurface process water control and will also serve to fulfill DEQ requirements for Site 12 as stipulated in the in situ mining permit. Such capabilities will then be available for application to other sites.



water control measures, and a program from the several steps portrayed in Figure 2 related to biological effects research. Biological subjects being studied at LETC encompass terrestrial (plants and microorganisms), aquatic, and animal systems (1). The animal studies are primarily concerned with examining the health risks of occupational exposure to process waters that may be accidentally encountered at field sites or in the laboratory. The terrestrial, aquatic, and animal studies were initiated to fulfill two needs. The first need was to determine the impacts, if any, of process waters associated with LETC in situ processing field experiments on the local ecosystems and their components. This need was raised in the Environmental Assessment prepared for LETC field projects (24) in accordance with regulations established under the National Environmental Policy Act (NEPA). Biological impacts likely to occur as a result of failure of a containment or evaporation pond typifies the kinds of concerns raised in the Environmental Assessment.

The second need was to obtain information that would assist in the development of control technology for process waters. The control of process waters, particularly those produced at the surface, is primarily based on the development of treatment systems capable of upgrading the quality of the waters to a level satisfactory for their intended end use. It is therefore necessary to determine possible end uses of water along with the development of treatment systems. As previously mentioned, excess waters produced during in situ processing should be considered as a commodity. A potentially valuable use of excess waters would be for land applications, such as for agricultural irrigation or for revegetation of disturbed sites. If this application is to be pursued, then it is necessary to determine the level of treatment required in order to produce a water acceptable for land application. Characterization of constituents in treated and untreated waters and evaluation of legal restrictions on the quality of waters intended for surface disposal are two activities which help to determine required treatment levels. Screening the response of potential target organisms to process waters at various stages of treatment is a third activity being conducted at LETC to assist in the definition of treatment requirements. Through such biological screening studies, it is possible to determine what solutes or fractions in process waters are primarily responsible for adverse effects. Once this is determined, the capability of treatment methods to remove these materials can be considered. The final evaluation of the efficacy of the selected treatment procedure can also be tested through biological screening studies. In this manner, the biological screening work at LETC assists in determining treatment requirements and in assessing treatment procedures for waters potentially to be disposed of in land applications. Biological studies pursued for this purpose are deemed to be as integral to the overall development of control technology as the analytical characterization studies.

## SUMMARY AND CONCLUSIONS

There are federal and state regulations on surface and subsurface water pollution. Emerging in situ fossil fuel technologies must be cognizant of these and develop process water control measures to insure compliance.

industry. This paper has illustrated the approach in effect at the Laramie Energy Technology Center to use in house field activities for advancement of process water control technology while insuring compliance with regulations.

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## INTRODUCTION

Wastewater can be generated by several different sources within a shale oil recovery facility. The volume and quality of the wastewater from a particular source is dependent on the location and characteristics of the oil shale processed and on the type and size of recovery system used. The pollution potential may be high as in the case of retort water, or low as in the case of irrigation quality groundwater pumped from a mining area. Inclusion of an upgrading facility at a shale oil recovery complex will also impact the volume and quality of wastewater generated. Above-ground retorting facilities may reuse all of the wastewater streams available for moisturizing spent shale, although this is not necessary for all processes. Since moisturizing of subsurface spent shale is not required for in situ operations, wastewater may be discharged at these sites. However, modified in situ operations could use wastewater for moisturizing spent shale if shale mined from the in situ zones is retorted at the surface. In situ operations generate retort water in approximately the same volume as that of the crude oil produced. Therefore, a 50,000 barrel per day in situ facility would generate about 2 million gallons (16,000 m<sup>3</sup>) of retort water per day. By comparison, an above-ground retort may generate only 200,000 gallons (1,600 m<sup>3</sup>) of retort water per day at the same level of oil production.

This paper addresses studies undertaken at Pacific Northwest Laboratory to assess current technology for the treatment and disposal of shale oil wastewaters to maintain acceptable water quality levels in the receiving waters of the oil shale regions presently under development. Although the shale oil industry is largely in the pilot plant/demonstration phase, the codevelopment of adequate wastewater control technology is necessary for several reasons: 1) prevent environmental damage as a result of the pilot plant/demonstration operations themselves; 2) control techniques may produce water which can be reused in the production process and this should be taken into account in the design of full-scale facilities; 3) adequacy of control technology should be fully assessed at an early stage to obviate delays and problems in construction and/or operation of full-scale production facilities; and 4) characterization of effluent discharges from pilot plant/demonstration operations will facilitate other environmental and health assessments. The major oil shale deposits in the United States are located in Colorado, Wyoming, and Utah. Therefore, developers of the shale oil industry must be fully cognizant of the importance of conservation of the limited water supplies in this area.

## LAND DISPOSAL

Land disposal of wastewater utilizes interactions between plants and the soil surface and matrix to achieve pollutant removal as the wastewater flows to the receiving water. Passage of the Federal Water Pollution Control Act PL 92-500 has focused attention on land disposal of wastewater as an alternative to be considered for complying with zero discharge requirements slated for 1985. Land

### Pollutant Removal Mechanisms

Removal of wastewater constituents is accomplished by physical, chemical, and biological processes with numerous and complex interactions occurring between these processes. The physical process of filtration provides the removal mechanism for suspended particulate matter in the wastewater. Soil and root microorganisms are responsible for biological degradation of numerous wastewater constituents. Both organic and in-organic compounds are broken down and/or utilized for metabolism by these microorganisms. Chemical processes, such as precipitation, ion exchange, oxidation and reduction, may occur to remove many inorganic and some organic substances. Precipitation of heavy metals, for example, is primarily responsible for removal of these constituents in soil, although ion exchange may be a contributing factor.

### Land Application Methods

Existing land treatment facilities can be classified according to two different basic design patterns based on differences in liquid loading rates, land area requirements, and the interaction of the wastewater with vegetation and soil. The first method, infiltration, uses soil as purification medium while the second, overland flow, uses the land surface as the purification medium. Infiltration is further divided into two categories, irrigation and infiltration-percolation, which typically involve low and high rates of application, respectively.

Irrigation is the most common method of wastewater application. This is generally accomplished by sprinkler or spray methods. In areas where irrigation water is scarce, the system is managed to provide the maximum return from a crop, whereas in areas of sufficient water supply, criteria allowing maximum hydraulic loading are followed. Revenue realized from a crop is used to defray operating costs so deciding whether the system is to produce crops or treat effluent is important. Controlling soil salts is vital for plant growth to prevent buildup of toxic concentrations. This is accomplished by managing the wastewater salt concentrations and the rates of application.

Care must be taken to avoid overloading the system which prevents further infiltration of the applied wastewater. The soil can become clogged and the formation of shallow ponds can occur resulting in anaerobic conditions. Anaerobic bacteria can create slimes of incompletely degraded organic matter and particulates which are effective soil surface sealants. Other factors that can cause clogging are: 1) compaction from heavy weight; 2) the movement of fine grains of soil down from the upper zones; and 3) the formation of insoluble compounds from reactions between wastewater constituents and soil water and/or minerals.

when investigating the applicability of land treatment and disposal for a particular wastewater. The general criteria for judging the suitability of a wastewater for land disposal are given below:

1. The organic material must be biologically degradable at reasonable rates.
2. It must not contain materials in concentrations toxic to soil microorganisms. Since some toxic materials may accumulate through adsorption or ion exchange and approach toxic levels after prolonged operation, there must be reasonable assurance that this effect can either be prevented or mitigated.
3. It must not contain substances that will adversely affect the quality of the underlying groundwater. In many instances, decisions relative to this aspect of land disposal systems are difficult because of the uncertain nature of available estimating techniques.
4. It must not contain substances that cause deleterious changes to the soil structure, especially its infiltration, percolation, and aeration characteristics. An imbalance of sodium ion is a common problem in this regard.

Characteristics relevant to land disposal are presented for a number of different retort waters in Table 1.<sup>(1)</sup> All of the retort waters, except that from the Utah in situ test site, are from simulated in situ retorts at the Laramie Energy Research Center and the Lawrence Livermore Laboratory.

High salinity commonly found in the retort water would be toxic to most cover crops. Waters having conductivities greater than 2,250  $\mu\text{mhos/cm}$  are considered unsuitable for irrigation in most cases. With the possible exception of one sample for which insufficient data are available (University of Southern California No. 1) none of the retort waters in Table 1 would be below 2,250  $\mu\text{mhos/cm}$  conductivity following ammonia removal by stripping. Steam stripping tests would be required to establish accurate conductivity values for the ammonia stripped water.

Substances which could affect groundwater quality at a land disposal site receiving retort water are listed below:

- high salinity;
- high nitrogen concentrations which yield nitrate on oxidation; and
- refractory organics which are not oxidized or removed by the soil.

The high salinity found in most retort waters would adversely affect drinking water quality groundwater if sufficient dilution were not available in the aquifer. A limit of 500 mg/l is recommended for drinking water and this value is exceeded by more than 100% for all the retort waters listed in Table 1, even after steam stripping for ammonia removal. Furthermore, evaporation of water during irrigation and leaching of salts from the soil will add to the dissolved solids content of the retort water as it percolates to the groundwater.

TABLE 1. Retort Water Quality Data Pertinent to Land Disposal

Constituents	10 Ton Simulated In Situ Retort Runs, LERC <sup>(2)</sup>						
	S-29	S-31	S-32	S-33	S-35	S-36	S-37
Na <sup>+</sup> , mg/l	210	1,300	1,200	160	530	960	150
K <sup>+</sup> , mg/l	8	70	47	70	23	23	21
Mg <sup>+2</sup> , mg/l	3.2	280	140	17	130	350	210
Ca <sup>+2</sup> , mg/l	0.6	9.8	4.9	4.9	27	29	35
NH <sub>3</sub> -N [includes NH <sub>4</sub> <sup>+</sup> ], mg/l	14,200	10,500	13,500	8,900	5,100	4,800	--
Total Alkalinity, mg/l CaCO <sub>3</sub>	40,800	34,000	47,000	20,500	17,200	13,900	8,200
Added Ca <sup>+2</sup> , (a) mg/l	3,900	1,420	440	4,460	400	1,300	--
Cl <sup>-</sup> , mg/l	5,000	4,200	3,200	7,900	2,300	4,600	1,100
SO <sub>4</sub> <sup>-2</sup> , mg/l	1,600	1,600	320	2,100	380	1,800	1,400
Total Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>+2</sup> , Ca <sup>+2</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , mg/l	10,700	8,880	5,350	14,700	3,790	9,140	3,736 <sup>(d)</sup>
Total Filterable Residue, 103°C, mg/l	--	--	--	--	--	--	--
Total Organic Carbon, mg/l	6,060	3,880	2,830	10,660	4,970	9,370	33,350
Biochemical Oxygen Demand, mg/l	--	--	--	--	--	--	--
Chemical Oxygen Demand, mg/l	--	--	--	--	--	--	--
Conductivity After NH <sub>3</sub> Stripping, (b) µmhos/cm	>2,250	>2,250	>2,250	>2,250	>2,250	>2,250	>2,250

	University of Southern California <sup>(3)</sup>		LERC 150 tonne Retort, LBL <sup>(4)</sup>	Lawrence Livermore <sup>(c)</sup> 7 Ton Retort	Utah in situ Test Site <sup>(c)</sup>
	No. 1	No. 2			
Na <sup>+</sup> , mg/l	312	--	655	164	3,500
K <sup>+</sup> , mg/l	3.5	--	37	28	90
Mg <sup>+2</sup> , mg/l	48.4	16.4	24	2.3	16
Ca <sup>+2</sup> , mg/l	14.9	4.6	3.3	1.5	<1
NH <sub>3</sub> -N (includes NH <sub>4</sub> <sup>+</sup> ), mg/l	4,790	--	8,360	25,000	3,060
Total Alkalinity, mg/l CaCO <sub>3</sub>	--	--	38,000	80,500	14,500
Added Ca <sup>+2</sup> , (a) mg/l	--	--	--	--	0
Cl <sup>-</sup> , mg/l	--	1,560	57	--	--
SO <sub>4</sub> <sup>-2</sup> , mg/l	59	930	1,100	--	--
Total Na <sup>+</sup> , K <sup>+</sup> , Mg <sup>+2</sup> , Ca <sup>+2</sup> , Cl <sup>-</sup> , SO <sub>4</sub> <sup>-2</sup> , mg/l	--	--	1,900	--	--
Total Filterable Residue, 103°C, mg/l	--	--	4,210	--	13,500
Total Organic Carbon, mg/l	3,182	19,000	4,980	--	--
Biochemical Oxygen Demand, mg/l	5,500	350	5,330	3,000	3,400
Chemical Oxygen Demand, mg/l	20,000	12,500	8,800	8,660	8,200
Conductivity After NH <sub>3</sub> Stripping, (b) µmhos/cm	--	--	>2,250	3,800 <sup>(d)</sup>	>2,250

(a) Ca<sup>+2</sup> added as Ca(OH)<sub>2</sub> for ammonia stripping; Ca<sup>+2</sup> mg/l = (mg/l NH<sub>3</sub> - N/14 mg/meq - mg/l Total Alkalinity/50 mg/meq) (20 mg/meq)

(b) Conductivity assumed to exceed 2,250 µmhos/cm when total ions exceed 1,200 mg/l.

(c) Analysis by Pacific Northwest Laboratory.

(d) NaOH added for stripping ammonia; conductivity measured on steam stripped water adjusted to pH 7.

concentration of ammonia, but other forms of nitrogen (nitrate and organic -N) may dictate the land requirement to attain the desired nitrogen loading. The nitrate and organic -N content of retort water has not been determined on a sufficient number of samples to establish an average or range of values.

Steam stripping of ammonia is more effectively accomplished at high pH levels. Stripping efficiency is reduced as neutrality is approached and becomes low for acidic solutions. Additional alkalinity in the form of lime is frequently added to maintain adequate pH levels. The addition of lime in the stripping process substitutes  $\text{Ca}^{+2}$  ion for ammonia ion which is beneficial from the standpoint of the ratio of  $\text{Na}^{+}$  to  $\text{Ca}^{+2}$  plus  $\text{Mg}^{+2}$ . However, if considerable lime is required, the salinity of the steam stripped waste will be high due to the calcium salts present. The alkalinity deficit reported as added  $\text{Ca}^{+2}$  (lime) for steam stripping is given for most of the retort waters in Table 1. Removal of all the ammonia may not be required since some nitrogen will be required for vegetation growth and oxidation of the organic matter in the retort water. In addition to ammonia, nitrogen can be supplied by organic-nitrogen and nitrate-nitrogen in the retort water.

The generally high ammonia levels in retort water would be expected to cause toxicity problems if not removed prior to disposal of the water to land. Although removal of the ammonia may be relatively costly, part or all of this cost may be recovered by marketing the ammonia. It is likely that steam stripping would be used to remove the ammonia since this process is well adapted to removal of high concentrations of ammonia from wastewater. Steam stripping is the standard industrial process used for removal of ammonia from coking liquors and petroleum refinery sour water. Sufficient alkalinity must be available in the retort water to allow conversion of  $\text{NH}_4^{+}$  ion to volatile  $\text{NH}_3$  which is stripped by the steam passing counter-currently to the water in the stripping column. Alkalinity and ammonia data on only one retort water, Utah in situ test site, indicate sufficient alkalinity to steam strip the ammonia. Addition of alkalinity would probably be required for the other retort waters. The total alkalinity reported for these waters cannot be considered an accurate guide, however since the end point pH for alkalinity titration may be well below pH 7. Ammonia stripping efficiency has not been adequately defined to date for assessing this aspect of land disposal. Furthermore, a pilot study may be required to accurately establish the optimal nitrogen loading.

It is possible that some of the organic constituents in retort water will be resistant to oxidation and might eventually be leached into the groundwater causing some deterioration in the quality of the groundwater. A low BOD relative to a COD could indicate a large fraction of the organic matter in the retort water is not readily biodegradable. Therefore, it is anticipated that low loading rates will be required to allow sufficient time for oxidation of the organics by the biota in the soil. The generally high organic content would appear to be the limiting factor on application rates of retort water to land rather than hydraulic characteristics. Furthermore, refractory organics which would not degrade even under low loading rates would leach through to groundwater.



or retort water. No data are available on the presence of organic substances which may cause problems.

Substances which cause plugging of the soil commonly include sodium ion (when it is unbalanced with  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ ) and suspended solids (nonbiodegradable). Suspended solids can plug the pores of the soil through the process of filtration, while sodium ion can cause dispersal of the clay particles in the soil thus sealing the pore structure. Currently, data are insufficient to evaluate the possible effect of suspended solids in retort water on land disposal, but at least part of the suspended matter in retort water is expected to be removed in the pretreatment steps for ammonia stripping to avoid fouling the stripping column. Air pollution from volatile organic constituents in this waste is also a potential problem. Retort water generally has an offensive odor which would not be well received by downwind recipients from the disposal site. Consideration would also have to be given to the possible presence of volatile toxic organics or other organics which would degrade air quality in the region.

### Effect of Climate

The long winters characteristic of the oil shale regions of Colorado, Utah, and Wyoming adversely affect the cost of land disposal by irrigation and overland runoff due to the large wastewater storage requirement. Irrigation and overland runoff are not possible during extended periods of freezing temperatures and application rates must be reduced during cool weather. Based on the length of frost free seasons, storage requirements range from 5 to 10 months, however, specific site operations may decrease the storage area needed.

## UNDERGROUND INJECTION

Underground or deep well injection is a disposal method which seeks to isolate a liquid waste in a geologic strata to eliminate, as nearly as possible, any environmental impacts resulting from disposal of the waste. Geologic strata selected to receive wastes by this method are generally located at a considerable distance from ground surface to provide additional assurance of confinement and avoid contaminating freshwater aquifers near the surface. Underground injection is normally reserved for wastewaters which are very difficult or expensive to treat for release to surface receiving waters. It is used extensively for the disposal of oil well brine wastes.

### UNDERGROUND INJECTION WELLS

A typical well consists of several pipes extending below the surface. The function of each of these pipes is as follows:

Conductor Pipe - This is the first of several concentric pipes that are placed into a disposal well. It extends between 30 and 60 m below the surface and prevents shallow water contamination while the surface hole is being drilled. This pipe is usually driven into place with a pile driver.

Surface Casing - This pipe extends from the surface to approximately 60 m below the base of the freshwater. This casing is cemented in place back to the ground

below the disposal zone, depending upon the type of completion intended. This casing is also cemented back to the surface and inside the surface casing. Its purpose is to seal off the formation above the disposal zone and below the freshwater.

Injection Tubing - This pipe is the conduit through which the effluent travels to the disposal zone. It is always sealed at the well head and usually just above the disposal zone. The annular space between the protecting casing and injection tubing is filled with a noncorrosive fluid. Pressure should be applied to this annulus approximately  $35,000 \text{ kg/m}^2$  higher than the injection pressure. The higher annular pressure will prevent any flow of effluent into the casing tubing annulus.

#### Disposal Zone Completion

If the well is completed in a sand formation, the gravel packed sand screen completion method should be used. If the well is completed in a limestone formation, open hole or perforated completions are acceptable.

#### WASTE CHARACTERISTICS

The suitability of waste for underground injection depends on its volume and physical and chemical characteristics, and on the physical and chemical properties of the potential injection zones and their interstitial fluids. Wastewater that is desirable for injection must be: 1) low in volume and high in pollutant concentration; 2) difficult to treat by surface methods; 3) free of any adverse reaction with the formation fluid or the strata; 4) free of suspended solids; 5) biologically inactive; and 6) noncorrosive.

Waste disposal into underground aquifers constitutes the use of limited storage space, and only concentrated, very objectionable, relatively untreatable wastes should be considered for injection. The fluids injected into deep aquifers do not occupy empty pores, but displace the fluids which saturate the storage zone. Consequently, optimal use of the underground storage space will be realized by the use of underground injection only when more satisfactory alternative methods of waste treatment and disposal are not available.

Reaction of the wastewater with the formation water or the strata is important. Resulting problems could include dissolving the formation, generating a gas or precipitate in the formation, and clogging by biological growths. The wastewater should be free of suspended solids and biologically inactive to avoid reservoir clogging. The corrosiveness of the wastewater should be low to prevent tubing and pump corrosion.

Retort water characteristics vary depending on the type of oil shale, retorting process, and retort operating conditions. As shown in Table 1, BOD<sub>5</sub> values range from 350 to 5500 mg/l and filterable residue from 150 to 101,000 mg/l. Ultrafiltration may be necessary to remove the suspended solids. Biocide addition may be necessary because high BOD concentrations promote biological activity.

Ammonia concentrations of retort water vary from 2600 to 31,500 mg/l. Toxic level of ammonia for anaerobic fermentation is 1300 mg/l (toxic level may vary considerably due to synergistic or antagonistic effects of other ions). High ammonia concentrations in the retort water should prevent biological activity. When ammonia concentration is reduced, (either by treatment for ammonia recovery or by ion exchange during migration of fluid in the disposal zone) the probability of biological activity is increased. If necessary nutrients (mainly Ca, Mg, and P) are present in the disposal zone, biological activity of the retort water is almost certain. Plugging of the injection zone by bacterial growth and by gas formation ( $\text{CH}_4$  and  $\text{CO}_2$ ) is likely to occur unless very long residence times in the injection zone are permitted for further reaction.

### DISPOSAL SITE SELECTION

Great care must be exercised in the selection of an underground disposal site for liquid wastes. The suitability of a specific location of a waste injection well must be evaluated by a detailed geological subsurface investigation. However, regional geological conditions can be used to evaluate general suitability of certain areas.

Certain areas of the continental United States, such as the Rocky Mountains, are generally unsuitable for waste injection wells because igneous or metamorphic rocks lie at or near the ground surface. Such rocks do not have sufficiently high porosity or permeability to warrant their use as a disposal formation. Areas with extensive extrusive volcanic sequences exposed are also not suitable for waste disposal wells. Even though these rocks have porous zones, they usually contain freshwater.

The final appraisal of a disposal well site is usually determined by a two-phase geologic investigation. The first phase includes an evaluation of potential sites on the basis of available data. The second phase consists of a more detailed evaluation of subsurface conditions based on information obtained from drilling a pilot hole or the injection well.

Information sought during the first phase of the investigation and prior to the installation of an injection well includes the extent, thickness, depth, porosity, permeability, temperature, water quality, and piezometric pressure of potential injection zones. The presence of impermeable confining beds, lateral changes in rock properties, the existence of faults or joints, and the occurrence of any mineral resource in the area must also be evaluated. Existing wells in the area which may penetrate the potential injection zones must be located because liquid wastes could escape through these wells if not properly plugged.

The second phase of the investigation is conducted during the drilling and testing of the injection well. Often the actual injection zone is not selected until the well has been drilled and a number of potential zones have been tested and until the chemical quality of water in the potential zones has been evaluated. Pumping tests are used to measure the permeability and water samples are obtained for chemical analysis. Other important rock properties are measured by geophysical logging, drill-stem testing tools, or by laboratory tests on core samples. The results of these geologic investigations are used not only in evaluating the feasibility of subsurface waste disposal, but also to provide basic data for designing the injection well and the optimal rate of injection.

Federal, state, and local agencies and industries to develop comprehensive programs to prevent or eliminate groundwater contamination and to improve sanitary conditions of these waters. In 1974, EPA issued "Administrator's Decision Statement No. 5" as agency policy on injection wells and subsurface emplacement of fluids by well injection. This policy was drafted to protect the subsurface from pollution or environmental hazards as a result of improper injection practices and poorly sited injection wells. Under this policy, EPA opposes the emplacement of wastes by injection without strict controls and a clear demonstration that such emplacement will not interfere with present or potential use of the subsurface environment, contaminate groundwater resources, or otherwise damage the environment. EPA can require that all proposals for subsurface injection be critically evaluated to determine that the following guidelines have been met:

- All reasonable alternative measures have been explored and found less satisfactory in terms of environmental protection.
- Adequate preinjection tests have been made for predicting the fate of materials injected.
- There is conclusive technical evidence to demonstrate that such injection will not interfere with present or potential use of water resources nor result in other environmental hazards.
- The injection system has been designed and constructed to provide maximal environmental protection.
- Provisions have been made for monitoring both the injection operation and the resulting effects on the environment.
- Contingency plans that will prevent any environmental degradation have been prepared to cope with all well shut-ins or well failures.
- Provisions will be made for plugging injection wells when abandoned and for monitoring plugs to ensure their adequacy in providing continuous environmental protection. Also under this policy, EPA acknowledges that subsurface injection of wastes is only a temporary means of disposal until new technology that will ensure a higher degree of environmental protection becomes available.

In December of 1974, the National Safe Drinking Water Act was passed by Congress. The purpose of this legislation was to ensure that water supply systems meet minimum national standards for the protection of public health. The Act was designed to achieve uniform safety and quality of drinking water in the nation by identifying contaminants and establishing maximum levels of acceptability. The major provision of the Act that encompasses the underground injection program is the establishment of regulations to protect the underground drinking water sources by the control of subsurface injection.

Various states are to have enforcement responsibility for groundwater protection. If a state underground injection control program is to be approved by EPA, it must:

- allow permits for underground injection only when the applicant can prove that injection will not endanger drinking water sources;
- provide for inspection, monitoring, record keeping, and reporting to EPA; and
- include no requirements that interfere with underground water or brine injection in oil or gas production, or for secondary or tertiary oil recovery, so long as freshwater aquifers are unaffected.

If a state does not have an approved underground injection control program, EPA should assume enforcement responsibilities.

In August 1976, EPA issued the proposed new 40 CFR Part 146 setting forth the regulations governing stage underground injection control (UIC) programs. The intent of this proposed regulation is to:

- establish minimum requirements for effective state programs to protect existing potential underground sources of drinking water from being endangered by the underground injection of fluids;
- provide improved protection of public health by controlling certain potential sources of underground drinking water contamination;
- provide minimal national control;
- allow a state to exercise maximum flexibility to develop programs to meet their needs, noting that differences exist between states, including geological conditions, use and availability of groundwater, and intensity of underground injection operations; and
- provide a program that would not be excessively costly to the states or to most injectors.

#### TREATMENT OF RETORT WATER

Bench-scale treatability studies are being conducted to evaluate current technology for the removal of pollutants from shale oil wastewaters. Retort waters generated by pilot plant and in situ test facilities are used in these studies to assess the adequacy of treatment processes to achieve the desired effluent quality. The wastewater treatment process selected for evaluation are essentially patterned after technology used by petroleum refineries.

#### EVALUATION CRITERIA

In the absence of sufficient waste treatment data to develop guidelines for disposal of retort or process wastewater to surface receiving waters, tentative evaluation criteria based on state standards are provided in Table 2. Except for total dissolved solids, these values are taken from water quality standards

1	BOD <sub>5</sub>	30 mg/l
2	Suspended Solids	30 mg/l
3	Oil and Grease	10 mg/l and no Visible Sheen
4	pH	6.0-9.0
5	Settleable Solids	Essentially Free From
6	Floating Solids	Essentially Free From
7	Taste, Odor, Color	Essentially Free From
8	Toxic Materials	Essentially Free From
9	Total Dissolved Solids	500 mg/l

Note: Numbers 1-4 above provide specific limitations for discharge of wastes not covered by other industrial effluent limitation guidelines in the State of Colorado. Numbers 5-8 are standards applicable to receiving waters for Colorado, Utah, and Wyoming. Number 9 is the average total dissolved solids in the Colorado River at Grand Valley, Colorado.

and effluent limitations for the states most likely to be involved in shale oil development (Colorado, Utah, and Wyoming). The limitation of 500 mg/l for total dissolved solids represents an average value for the Colorado River at Grand Valley, Colorado, which is in the vicinity of several planned commercial shale oil recovery operations. Discharges of effluents containing more than 500 mg/l TDS into the Colorado River in this area could ultimately increase the salinity above control limits for this river as it crosses the border into Mexico. Total suspended solids for retort waters listed in Table 1 exceed 500 mg/l with but one possible exception (USC No. 1) after ammonia removal. Discharge of retort water to surface receiving waters is, therefore, unlikely without desalination.

Four out of five BOD values listed in Table 1 are two orders of magnitude or greater than the effluent limitation of 30 mg/l given in Table 2. It is unlikely that a practical biological treatment scheme could meet this limitation, however, subsequent chemical coagulation, sedimentation, filtration, and activated carbon sorption should achieve a very high level of removal. If this sequence of treatment processes cannot meet the limitations presented in Table 2, less stringent criteria may be applied. In some areas more stringent criteria may be necessary to protect local surface receiving waters.

Retort water can potentially contain several toxic materials. Ammonia, which is highly toxic to fish and other aquatic organisms, is present at relatively high concentrations. Most of the ammonia must be removed before biological treatment can be used to degrade organic material contained in this waste. Arsenic is also present at several mg/l in some retort waters and could interfere with biological treatment. Furthermore, removal would be required prior to discharge to surface waters. Other unidentified substances (e.g., organic substances) could also cause toxicity problems in biological treatment or in surface receiving waters.

## BENCH-SCALE TREATABILITY STUDIES

### Steam Stripping

Bench-scale studies were conducted to evaluate steam stripping as a means of removing ammonia from retort water. The steam stripper used in this work consisted of a two-inch ID glass pipe packed to a depth of four feet with 1/4-inch ceramic saddles. Feed to the stripper is introduced at the top of the column of saddles and is counter-currently contacted with steam generated by a reboiler at the bottom of the column. Steam, containing volatile constituents stripped from the feed, is removed from the top of the column, condensed, and collected in a condensate receiver. The condensate receiver is vented to a water trap and an acid trap in series to absorb ammonia vapor carried over with non-condensable gases. The steam stripped feed collects in the reboiler and is drawn off continuously to maintain the desired liquid level in the reboiler. Two operational modes were evaluated, one with recycle of the condensate and one without recycle. The condensate is recycled by injecting it into the feed stream to the stripping column. Recycle of the condensate eliminates the necessity of dealing with a separate wastewater stream but also reduces the efficiency of ammonia removal in the stripping column by increasing the ammonia concentration in the feed streams. The alternative of no condensate recycle results is an aqueous ammonia solution which contains volatile organic matter stripped from the retort water.

The steam stripping studies were performed using a sample of retort water from an in situ operation in Utah which contained 3100 mg/l ammonia. Ammonia removal with recycle of the condensate averaged 90% for 2 runs at a boiloff rate of 4.5%. Over 99% of the ammonia was removed without recycle of the condensate at a boiloff rate of 5.3%. Steam stripping also reduced the alkalinity from 14,300 mg/l to about 4,700 mg/l. However, the pH of the retort water increased from 8.8 to about 10 because of carbon dioxide stripping. Excessive foaming occurs in the reboiler which requires precise liquid level control to prevent the foam from entering the column where it causes flooding.

Some fouling of the packing in the stripping column was observed, which may have been the result of suspended matter depositing on the packing. Although settled retort water was used, it contained about 150 mg/l of suspended solids, which were reduced to about 30 mg/l through the stripper. A small volume of light oil was also removed by the steam stripping operation. Organic carbon removal by steam stripping ranges from 15 to 20%.

A sample of retort water from the Lawrence Livermore Laboratory (LLL) was steam stripped while operating in the condensate recycle mode at a condensate temperature of  $85.5 \pm 3.5^{\circ}\text{C}$ . The ammonia was reduced by 99.5% from 26,500 mg/l to 135 mg/l at a boiloff rate of 15% of the combined feed and condensate recycle. This boiloff rate is equal to 18% of the feed flow alone. Approximately 1/4 of the ammonia was recycled with the condensate stream and 3/4 was evolved from the condensate receiver as a gas. The feed flow to the stripper column with the LLL retort water was restricted to about half that of in situ test site retort water to avoid flooding in the column. This is believed to result from a greater gas flow ( $\text{CO}_2 + \text{NH}_3$ ) up the column with the LLL retort water.

at the Lawrence Livermore Laboratory, one from an above-ground retort in Colorado, and the other three samples from an in situ test site in Utah. Both aerobic and anaerobic biological treatment processes have been evaluated on a bench-scale. Aerobic treatment consisted of activated sludge or combined roughing filter (trickling filter) and activated sludge. The results of the aerobic treatment studies indicated toxicity problems in the treatment units as the concentration of retort water was increased in the feed to the units. Good biological growth and organic carbon removals were observed during the initial phases of the acclimation period but an apparent toxicity problem develops as the percent actual retort water in the feed increases and the percent artificial retort water decreases. Analysis of the retort water for toxicants revealed the presence of arsenic and thiocyanate. Thiocyanate is not believed to be a problem since the concentration of this constituent is below the threshold value of 500 mg/l for activated sludge. Arsenic could be a problem since it exceeds the threshold value of 0.1 mg/l for activated sludge. The Livermore sample contained 1.3 mg/l arsenic and the remaining samples contained 4-13 mg/l arsenic. Results of anaerobic digestion studies conducted with 3.5 liter digesters also indicated toxicant problems. Gas production from the digesters diminished steadily as the concentration of actual retort water was increased.

Results of studies to evaluate powdered activated carbon addition to the anaerobic digesters indicate successful operation in the case of the Livermore retort water, but continued toxicity problems with the other retort water samples. The powdered activated carbon is effective for removing certain soluble organics, including toxic organics, from solution which could reduce the stress on microbial population in the digesters. The activated carbon is also effective in some instances for removing heavy metals from solution, but its effect on arsenic in retort water is unknown at the present time. Analysis for soluble arsenic in the digester receiving in situ test site retort water revealed 0.96 mg/l which is near the toxicity threshold for anaerobic digestion. Soluble arsenic in the digester receiving Livermore retort water was 0.56 mg/l. Preliminary results indicate that activated carbon treatment of Utah in situ retort water will permit aerobic biological degradation to take place although the amount of activated carbon needed may be relatively high.

#### MINEWATER TREATMENT

Water pumped from underground oil shale mines or in situ operational zones in an oil shale formation may contain pollutants, such as fluoride, boron, and high dissolved salt concentrations, which will prevent unrestricted release of this water to surface receiving streams. Treatment and disposal technology for these minewaters is also being assessed.

#### FLUORIDE REMOVAL STUDIES

Treatability studies were conducted to evaluate methods for removing fluoride and boron from minewater. The results of bench-scale experiments with groundwater taken from a site in Colorado show a 50% breakthrough capacity of 350 bed volumes for fluoride removal by activated alumina adsorption. The groundwater fluoride concentration was 20 mg/l; therefore, the fluoride capacity is approximately 7 g/l of activated alumina. In order to achieve effective fluoride



to the feed at the beginning of the exhaustion cycle to neutralize the residual caustic regenerant in the bed. The acid addition for pH adjustment of the feed is expected to represent a substantial portion of the chemical cost of treatment for fluoride removal by activated alumina adsorption. An estimated 13¢ per thousand gallons of groundwater would be required to adjust the pH with sulfuric acid priced at \$50 per ton of acid. Regenerant costs are estimated to be 16¢ per thousand gallons of groundwater treated based on sodium hydroxide priced at \$280 per ton.

Results of precipitation experiments with simulated groundwater indicate 90% fluoride removal with phosphoric acid and lime addition. Approximately 9 moles of phosphorus and 10 moles of calcium per mole of fluoride are required to achieve this level of fluoride removal which would be needed to allow discharge of the groundwater to nearby surface receiving waters. The precipitation formed is basically a mixture of fluorapatite,  $\text{Ca}_5\text{F}(\text{PO}_4)_3$ , and hydroxy apatite,  $\text{Ca}_5(\text{OH})(\text{PO}_4)_3$ . The cost of phosphoric acid and lime to treat the groundwater is estimated to be about \$2 per thousand gallons, which is excessive relative to other treatment methods.

Ion exchange with a weak base anion exchange resin was investigated as a unique process which showed some potential because of the low selectivity of this resin for bicarbonate, the principal ion competing with the fluoride. Laboratory results showed a correspondingly low selectivity for fluoride which negates possible advantages this process may have over other ion exchange processes.

#### BORON REMOVAL STUDIES

Boron removal from the groundwater is not effected by either activated alumina or lime and phosphate treatment. Bench-scale studies with a boron selective ion exchange resin indicate good boron removal from 2000 bed volumes of groundwater containing 0.6 mg/l. Boron removal to less than 0.3 mg/l is required for discharge to nearby surface waters.

#### SUMMARY AND CONCLUSIONS

Current data in the literature indicate that the salinity of retort water from shale oil recovery operations will be too high in most cases for irrigation of cover crops needed for effective stabilization by land treatment and disposal. Furthermore, large storage lagoons would be required to hold the retort water during the long winters encountered in the oil shale regions of Colorado, Wyoming, and Utah. Additional problems which may arise with land disposal include air pollution from volatile constituents and groundwater pollution from refractory organics and dissolved salts in the retort water.

Regulatory restraints are expected to limit the use of underground injection for disposal of highly polluted shale oil wastewaters. Proof of confinement of injected wastes will be required to assure protection of drinking water resources, and this is often difficult and costly to accomplish. Underground injection of wastewater is a viable disposal option, however, where all reasonable alternatives have been explored and found to be less satisfactory in terms of environmental protection.

Fluoride removal from minewater with activated alumina and fluorapatite precipitation was investigated. Reagent costs for the precipitation were estimated to be \$2 per thousand gallons whereas reagent costs for activated alumina treatment were only 29¢ per thousand gallons. Boron was effectively removed by ion exchange on a boron specific resin.

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## INTRODUCTION

In modified in situ (MIS) oil shale retorting, the resource is processed in the ground. Porosity is introduced into the formation by mining out from 20 to 30% of the in-place oil shale. This material is brought to the surface and either processed in surface retorts or stockpiled. The balance of the material is rubblized underground using various mining techniques. Oil is extracted by pyrolysis and combustion.

This process produces oil, a low BTU gas and process water and leaves behind large underground chambers (retorts) of spent shale and surface piles of raw or spent shale. The acceptability of MIS retorting may depend on the resolution of several environmental issues related to these residuals including groundwater disruption, resource recovery, retort stability and solid and liquid residual disposal.

The purpose of this paper is to investigate the feasibility of returning the solids stockpiled on the surface and process water to the abandoned underground chambers. We believe that potential environmental problems can be largely overcome by returning on-site waste materials to the abandoned underground retort. This would fill the void space created by mining, thus improving structural strength and reducing permeability to groundwater flow. If sufficient strength could be developed, it may be possible to design retorts so that the pillars could be retorted and resource recovery improved. It would also result in the simultaneous disposal of solid and liquid residuals.

## CONTROL STRATEGY

Various materials could be introduced into an abandoned retort or surrounding strata to increase structural strength or to reduce the flow of groundwater through the retort. These materials, called grouts, have been widely used in a number of fields including oil field reservoir engineering, nuclear waste containment, gas storage in underground formations, deep coal mining, soil consolidation and various construction activities. The nature of these conventional materials needs to be explored to determine the types of grouts that may be produced from on-site waste materials and properties required for retort sealing.

tion of local ground water or surface water.

- (2) The grouting material must be chemically stable in the presence of saline groundwater.
- (3) The grout viscosity must be low enough and the setting time long enough for the slurry to penetrate a large area.
- (4) The grouted area should be able to withstand both hydrostatic and overburden pressures. The hydrostatic pressure is due to natural head differences that exist between the aquifers surrounding the oil shale deposits in some areas and to significant dewatering during retorting.

An impressive array of commercially-available grouting materials has been used in other industries. These have been extensively described in the literature (1, 2) and include cement and chemical grouts. Cement grouts typically have long setting times, are non-Newtonian and have relatively high viscosities compared to chemical grouts. Chemical grouts are water solutions of various inorganic or organic compounds and are most typically based on sodium silicate, acrylamide, polyphenolic and urea-formaldehydes, lignins, and resins. Properties and cost factors for some of these grouts are compared with spent shale in Table 1. Preliminary estimates indicate that it could cost from 20 to 270 dollars per barrel of oil for the grouting material alone if abandoned retorts were sealed with these conventional materials. Spent shale grouts, on the other hand, may be economically feasible if technical problems associated with their use are resolved.

The high costs of conventional grouts and the on-site availability of some of the raw materials necessary to manufacture them, suggests that waste products be used to produce grouts. Readily available materials include raw and spent shale, latent heat within the retort, gases, process water and mine water. These materials should be considered as raw materials for on-site manufacture of grouts that would not be economically competitive if purchased from commercial sources. Many of these components show promise for use as grouting materials. Some possibilities include on-site conversion of raw or spent shale into a pozzolan or cement, use of  $\text{NH}_3$  in the gas and process water to produce urea-formaldehyde polymers, use of  $\text{CO}_2$  in the gas and  $\text{Na}_2\text{CO}_3$  in the process water to produce insoluble carbonate deposits, and the manufacture of silica gels from mine water, retort waters or offgas.

There are many possible solutions to the retort abandonment problem using these on-site waste products. The most appropriate one will depend on desired strength increase, permeability reduction, retort/aquifer geometry and cost. The following sections of this paper will discuss the use of spent shale and process water as major components of a grout and methods of distributing the grout in the retort.

Table 1. Comparison between conventional grouting materials and spent shale

Class	Example	Viscosity before gelling, cp (range)	Gel time min. (range)	Cost factor relative to neat cement	Potential Application	
					Hydraulic barrier	Provid- tural Medium
Cement	Portland cement slurry (neat)	(a)	10-300	1.0	x	x
Silicate	Water glass (sodium silicate)	1.5-2	0.1-60	1.3	x	x
Polymer	Injectrol G (3)					
	AM-9 polyacrilamide (1)	1.2-1.6	0.1-300	7.0	x	x
Resins	PWG (3)	1.5	->300	9.0	x	x
	Herculox (3)	13	4-60	4.5	x	x
	Epseal (3)	80-90				
Emulsions	Asphalt 65% (4)				x	
Foams	Polyurethane foam (5)		15	1.5	x	
Spent shale	Lurgi (6)	(a)	28 days	0.05		
Lignin base	Blox-All (2)	8-15	3-90	1.65	x	
Unsaturated fatty acid	Polythixon FRD (2)	10-80	25-360		x	
Elemental sulfur		7 cp @ 159 C	sets when cool	available at low cost from gas refining sites		
Formaldehyde base	Urea-formaldehyde (2)	3.5-13	1-60	6.0	x	

(a) Depends on the water-cement ratio (WCR) and presence of additives. With a WCR of 45%, and no additives, the viscosity of cement is 200 cp. Addition of a slurry fluidizer (i.e., naphthalene polymer) may reduce this to 20 cp. By comparison of 450% to 900% is needed to reduce the viscosity of Lurgi spent shale to 200 cp.

strength-forming material (7). The comparison shows that spent shale compared with pozzolans in Table 2. This comparison shows that spent shale appears to meet the chemical requirements for ASTM Class C pozzolan and is very similar to natural pozzolans. This is of considerable interest because the spent shale could be used to reduce permeability and provide strength development of an abandoned MIS retort.

Two studies have been conducted on the use of surface spent shale to manufacture a cement-like material. However, these have met with limited success (possibly due to low temperatures reached in the surface retorts). Culbertson, Nevens and Hollingshead (7) studied the stabilization of spent shale from a TOSCO retort. Shear strength and confined compressive strength in the range of 250 to 500 psi were obtained. Strength development was positively correlated with the amount of cohesive hydrates formed. After 15 days of setting, no loss of strength occurred in samples resaturated with water.

Nevens, Habenicht and Culbertson (6) studied the filling of a simulated in-situ retort with a slurry of Lurgi spent shale. Samples calcined at 750 to 850 C required from 500 to 1000 wt % water to reduce the viscosity to 100 cp. Compressive strengths obtained after 28 days ranged from 5 to 200 psi.

Although results with 100% spent shale grouts have been discouraging to date, research is in its infancy and advances may occur. The most promising possibility is to use spent shale to create a hydraulic lime-pozzolan mortar. This is a mixture containing active lime (CaO) and pozzolanically active silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) which yield cohesive hydrates when mixed with water. This strategy is explored here by contrasting the chemistry of cements, pozzolans and mineralogical changes that occur during oil shale retorting.

#### Cement, pozzolan and oil shale chemistry

The chemistry of pozzolan and cement and of the carbonate/silicate minerals in oil shale is germane to understanding the potential role of spent shale as a grout. Cements are prepared by blending proper proportions of finely ground limestone and clay and firing the mixture in a kiln at 1450 to 1550 C. The resulting clinker is cooled, about 5% to 6% gypsum is added as a set retarder and the mixture is pulverized. When water is added to this material and the paste is allowed to set it will gradually convert to a hardened product. This process can be represented by the following set of chemical equations:

##### Calcining

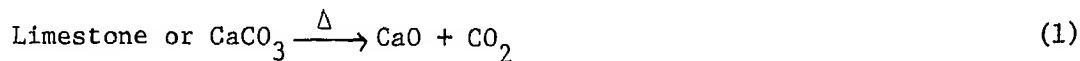
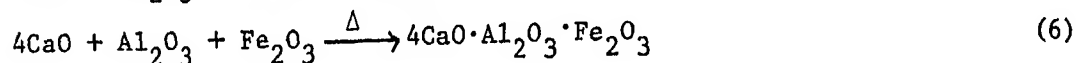
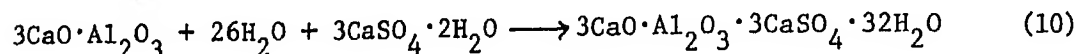
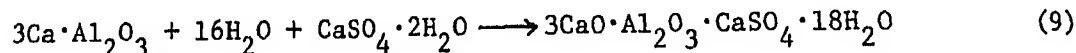
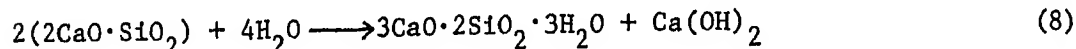
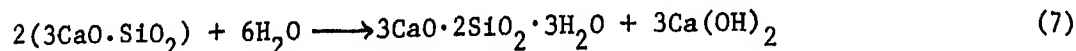


Table 2. Composition of pozzolans and spent shale

Constituent	Oxide analysis, weight percent				ASTM C-618-78 class C pozzolan (11)
	typical natural pozzolan (9)	typical industrial pozzolan (lignite fly ash) (10)	combustion run spent shale		
SiO <sub>2</sub>	55.0	28.7	46.5	)	
Al <sub>2</sub> O <sub>3</sub>	17.7	12.0	10.7	)	>50.0
Fe <sub>2</sub> O <sub>3</sub>	3.5	6.8	4.2	)	-
CaO	3.2	40.5	17.2		-
MgO	1.0	7.4	7.8		-
SO <sub>3</sub>	-	2.5	-		<5.0
FeO	0.9	-	-		-
K <sub>2</sub> O	6.4	-	3.0		-
Na <sub>2</sub> O	3.4	0.6	3.3		-
Loss on ignition	6.3	0.4	1.6		<6.0

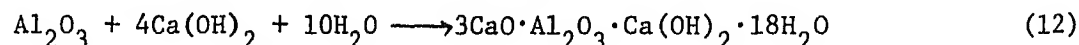
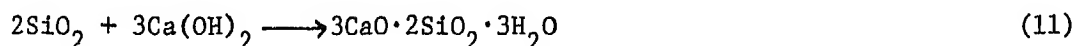


#### Hydration



It would not be economically feasible to manufacture cement on site because of the high energy requirements (8). However, a hydraulic lime-pozzolan could be produced at temperatures much below clinkering temperatures.

Pozzolans are siliceous and aluminous materials that react with lime in finely divided form and in the presence of moisture to form cohesive hydrates. These hydrates are the main strength-giving compounds of hydrated cement. Typical pozzolanic reactions are:

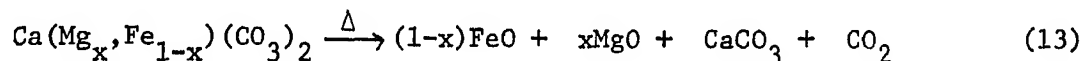


These equations show that if active silica and alumina react with lime, calcium silicate and calcium aluminate hydrates are formed. These compounds are similar to those that give strength to portland cement. The ability of a siliceous or aluminous material to react at normal temperature as shown is called "pozzolanic activity" and is measured by ASTM Method No. C 311-77 (11). A sufficient degree of pozzolanic activity may be present in spent shale or it may be increased by heat treatment, or by modifying retorting conditions, or by lime addition.

If pozzolanic activity could be induced in surface spent shale by modifying retort operating conditions, it may be possible to manufacture a hydraulic lime-pozzolan on site. This is more attractive than formation of a cement since activation of silica and alumina takes place at lower temperatures than the formation of clinker compounds (900 - 1000 C). For maximum development of cementitious properties, additional lime may be required. This could be added before retorting or afterward. Fine grinding of the spent shale would be required. Because the clinker compounds of portland cement, formed in equations (3) through (6), would not be present, the grout would set more slowly and have a lower final strength.



on the partial pressure of  $\text{CO}_2$ . Above 1000 C the calcium oxide reacts with silica to produce calcium silicate compounds ( $3\text{CaO}\cdot\text{SiO}_2$ ,  $2\text{CaO}\cdot\text{SiO}_2$ ) and other nonreactive compounds (gehlenites and akermanites). These reactions are summarized as (12):

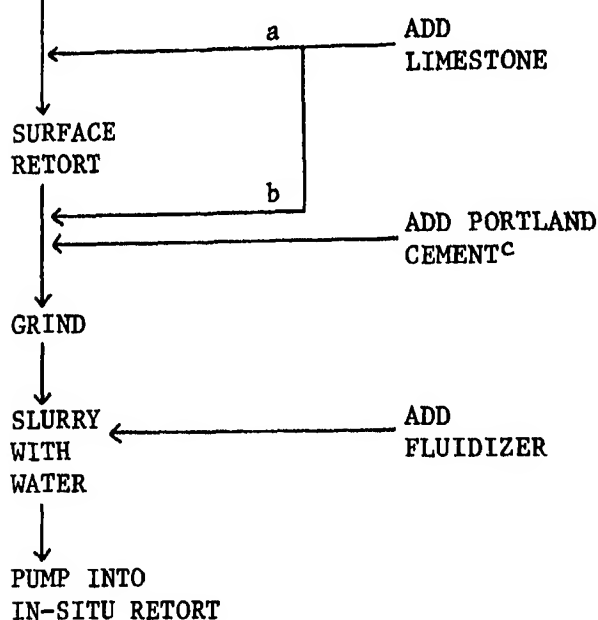


The temperature at which these reactions occur is very important in considering the use of oil shale as a cementitious material. Most surface retorts operate at less than 600 C, which is too low to form a mixture of active silica and active alumina with cementitious properties. Therefore, if spent shale is to be produced for use as a grouting material, the surface retorting process may have to be optimized for pozzolan formation as well as for oil yield.

Based on the foregoing, we propose that the surface retort be operated to produce a hydraulic lime-pozzolan mixture. This recommended strategy is summarized in Figure 1. This figure shows pozzolan production and additives that are being explored in an experimental program. The surface retort is operated to produce a hydraulic lime-pozzolan. The effect of additions of limestone, portland cement and slurry fluidizer are being investigated. The limestone addition would enhance the availability of lime to form cohesive hydrates. If strength of the lime-pozzolan mixture is inadequate, a small addition of portland cement may be desirable. The portland cement would contribute tricalcium ( $3\text{CaO}\cdot\text{SiO}_2$ ) and dicalcium ( $2\text{CaO}\cdot\text{SiO}_2$ ) silicate, which, upon hydration, yield  $\text{Ca}(\text{OH})_2$  and cohesive hydrates. The spent shale pozzolan would react with the  $\text{Ca}(\text{OH})_2$  as it is formed to yield additional cohesive hydrates as shown in equations (11) and (12). The slurry fluidizer would decrease the viscosity of the slurry so that it could be more easily distributed in the abandoned retort.

#### GROUT DISTRIBUTION

Grout distribution in abandoned retorts will depend on several factors including grout properties, retort properties and emplacement geometry. Most commercial grouting is performed by point injection from small diameter pipes placed in a grid pattern on centers less than 20 feet apart. This would not be economically feasible due to the large number of deep holes that would have to be drilled. Well spacing greater than or equal to 70 feet



- a Add limestone before retorting if retorting temperature is high enough to calcine limestone.
- b Add calcined limestone after retorting if retorting temperature is not high enough to calcine limestone.
- c Portland cement addition only if strength development without it is inadequate.

would be needed to make grouting attractive as a method of spent shale disposal if drilling were done from the surface. The effects of the geometry of the grout emplacement, the retort permeability and grout viscosity on retort groutability need to be studied.

Viscosity is the most important grout property for distribution. Spent shale slurries investigated to date have typically had viscosities of 500 to over 1000 cp at low water contents (100% by weight water added) (6). These slurries have generally had viscosity reduction to 50 cp at 200% by weight water added but some slurries have required 1000% by weight water to obtain viscosities less than 100 cp (for comparison, the viscosity of water is 1 cp at 20 C). The relative penetrability of spent shale grout will be strongly dependent on obtaining a low viscosity product (< 50 cp) at low water content (100% by weight water) to achieve desired strength development and permeability reduction.

Permeability of the spent in-situ retort will be the most important property for grout distribution. Uniform penetration of a particulate grout (e.g. spent shale-based grout) may be difficult to achieve because of the heterogeneous nature of the void space of an abandoned in-situ retort. It includes large voids between rubble fragments (up to one inch and more), fine voids where oil shale has been fractured but fragments have not moved apart, fissures and cracks in retort walls, and minutes pores created in spent shale by pyrolysis of kerogen. Invasion of only the larger pores may not be adequate to reduce permeability.

Effective grouting may require complete and uniform penetration of most voids. This will be controlled by the relative size of particles in the grout and the void space in the rubble. In order to penetrate a retort at a reasonable pressure and flow rate, the size of the largest suspended particle should not be greater than about one-third of the size of the voids. Typically, particulate grouts are used for openings that are 1/16 inch or larger and chemical grouts are used for openings that are less than 1/16 inch. Therefore, two injections may be required to seal an abandoned in-situ retort. The first would use a grout with a relatively large particle size and the second would use a nonparticulate grout.

Point source grout injection may not be very effective for grout distribution in abandoned retorts. The grout penetration from a point source is severely limited by the high headloss developed near the tip of the pipe. For most commercial grouts however, set up time is short and point sources are used because not enough grout penetration occurs prior to set up for the well point headloss to become a problem. However, for abandoned retorts, this configuration is not suitable as a large number of injection ports would be required. The cost for this may be excessive. Therefore, line source placement should be explored.

Line source injection is beneficial for increased rubble penetration and faster grout distribution but it is limited by the size of the pipe available to deliver the grout and head required to push the grout through the rubble. A 36 inch pipe diameter flowing at 2 ft/sec could deliver 14 cfs of grout to the rubble. If this grout were delivered to a slotted section approximately 50 feet in length, approximately 8 hours would be

This paper considered the production of a hydraulic lime-pozzolan mixture from spent shale produced in surface oil shale retorts. This mixture could be slurried with process effluents and pumped into abandoned MIS retorts. This control strategy would simultaneously provide for long-term retort stability, minimal groundwater disruption, enhancement of resource recovery and disposal of process residuals. Work completed to date and some theoretical considerations suggest that surface retorts can be operated to produce a spent shale with pozzolanic properties. Additions of limestone, portland cement and slurry fluidizer may be required. Additional work is required to determine optimum retort operating conditions and required additives, and to resolve a number of technical problems. Preliminary cost estimates indicate that this would be an economically viable strategy if technical issues could be resolved. These include high grout viscosities, high water-solid ratios, poor strength development and grout distribution within an abandoned retort. If spent shale grout or some other low-cost on-site waste material cannot be reclaimed for retort filling and plugging, it is possible that MIS retorting may not be both environmentally and economically viable due to the high costs associated with other control strategies. However, if the constraint of enhanced resource recovery is relaxed and if it can be demonstrated that creep and subsidence are not long-term problems, then other lower-cost control strategies may be considered. These would address only the groundwater disruption issues and would include leaching, mine design modifications, grout curtains, and chemical immobilization of leachables.

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## ABSTRACT

The injection of wastes into deep underground formations is the most economical method for disposal of liquid wastes that are not amenable to surface treatment. Operating costs are lower for pretreatments and subsurface disposal than for surface treatment systems, and plant area requirements are fewer. Chemical treatment is minimal, and generally the only physical treatment required for underground injection is filtration. This report presents a broad view of modern industrial underground waste injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

The petroleum industry has been injecting fluids into subsurface formations for many years; therefore, many of the techniques and much of the equipment for handling industrial liquid wastes are already available for industrial waste disposal. The techniques for drilling and completing the disposal wells have been perfected, and the necessary equipment is available. Similarly, the behavior of fluid flow through porous rocks and unconsolidated sand has been investigated. Therefore, many of the theories and equations describing the fluid distributions have been proved. Modification may, however, be needed to make them applicable to waste injection systems and to describe the chromatographic properties of the injected wastes constituents.

A subsurface disposal system can be successful only if a porous, permeable formation of wide areal extent is available at sufficient depth to ensure safety in storage and retention of the injected fluids. The wastes usually are treated for solids removal and compatibility with the formation. An impermeable zone, such as shale or evaporite, must overlie the injection horizon to prevent vertical migration of the waste or displaced formation brines into low-salinity aquifers above the disposal zone.

underground waste-injection systems and their operations. The types of wastes being injected and the major features of equipment, geologic formations, and well operation are described.

Almost any specific waste-disposal problem can be resolved with modern industrial technology, but the processes for waste treatment and disposal are limited by practical economics. The injection of liquid wastes into deep geologic formations is becoming increasingly important. This method is being used especially in the major oil-producing states, where the technology of fluid extraction from, and injection into, underground formations was developed and has been in use for about 50 years.

The experience of the petroleum and chemical industries has shown that underground injection is applicable to all types of liquid wastes, (e.g. mineral and organic acids, bases, inorganic salts, oxygenated and chlorinated hydrocarbons, and mixtures of many other types of compounds).

Subsurface formations have extremely large adsorptive surfaces and contain a diverse population of anaerobic bacteria; both of these factors are beneficial in containing and decomposing the injected wastes. In addition, salts contained in subsurface brines and the diverse chemical constituents of host rocks serve as buffering agents and chemical reactants to aid in the conversion and decomposition of the waste compounds.

If deleterious waste compounds are, indeed, irreversibly adsorbed and decomposed to harmless compounds, the environmental impact of underground waste storage is significantly less than that of chemical waste disposal by burning or discharging to surface streams or the ocean. However, present limitations of knowledge of the possible reaction of waste constituents with subsurface formations impose a potential for creation of an environmental hazard.

#### TYPES OF WASTES

The selection of subsurface waste disposal as a means of disposing of wastes is based on: (1) the difficulty of treating the waste to an acceptable level of purity for reuse or for discharge to surface streams and (2) the economic margin, if any, between subsurface waste disposal and surface treatment methods.

Some wastes are corrosive acidic or brine solutions of inorganic constituents; some are basic wastes that readily form insoluble hydroxides and other precipitates when mixed with other

considered. Thus, each system is unique, and each system is designed to process a specific waste mixture for injection into a particular geologic formation.

In this report, the types of wastes being injected into underground formations are classed in three distinct categories: produced oilfield brines, inorganic industrial wastes, and organic industrial wastes, as shown in Tables 1, 2, and 3, respectively. Each of the three types of wastes is subdivided on the basis of the individual waste constituents or of some outstanding property such as pH.

### Oilfield Brines

In some oil fields being produced by waterflood, the brine produced with the oil is reinjected into the oil-producing formation for displacement of crude oil. Thus, the brine that would otherwise be a waste product is used for additional oil recovery and economic gain. Additional quantities of water required for a waterflood project are usually obtained from brine wells completed in formations above or below the oil zone.

However, just as many oil fields are being produced by other mechanisms that do not require the injection of brine into the oil-producing formation. In these fields the produced brine is a waste product which is disposed of by injection into subsurface formations from which no fluids are withdrawn. Thus, this operation is similar to the injection of liquid wastes by the chemical industry.

Oilfield brines have a wide range of concentrations of a large variety of cations and anions. Concentrations range from less than 100 ppm to more than 100,000 ppm, as shown in Table 1, where the brines are classified according to the cation and anion in greatest concentration. Most of the produced brines have sodium or calcium chlorides as their major constituents, but magnesium, bicarbonate, and sulfate ions predominate in some. Other ions are present as minor constituents, and in some brines, ions such as bromine and iodine are present in commercially economic quantities (5).

Concentrations of ions from waters of different geologic formations, and in places even at different sites within the same formation, differ widely. Consequently, there are no typical oilfield brines, and generalizations of the chemical reactivity of different brines cannot be made. However, some problems



TABLE 1. - Analyses of Natural Groundwaters Showing Major Constituents of Various Types of Brines (ppm)

Type of Brine	Formation	Location	Na	Ca	Mg	Cl	HCO <sub>3</sub>
Sodium chloride	Big Injun	Pa.	52,200	1,730	3,910	121,000	70
Sodium carbonate	Ellis	Mont.	3,140	90	80	2,890	4,040
Sodium sulfate	Coalinga	Calif.	3,290	390	340	2,520	360
Calcium chloride	Arbuckle	Kans.	4,230	16,900	8,430	60,100	42
Calcium carbonate	Embar	Wyo.	140	140	30	10	210
Calcium sulfate	Madison	Wyo.	580	870	180	1,070	1,080
Magnesium chloride	Lodgepole	Manitoba	44,900	3,260	67,340	94,900	2,140
Magnesium carbonate	Uinta	Colo.	450	428	542	90	1,185
Magnesium sulfate	---	New Mexico	100	1,000	25,000	9,000	0

1. Precipitates: Oxidation of brine constituents causes closed system, atmospheric oxidation of brine constituents causes the precipitation of salts and hydroxides. Complete removal by filtration is too costly; therefore, aeration equipment is used to complete the oxidation, which is followed by sedimentation and filtration.

Closed systems are used to keep the brine in essentially the same condition that existed in the formation. The closed system is more economical to operate and requires less surface equipment than the open system because the need for aeration and sedimentation is eliminated. Brine is removed from the oil-water separator, filtered, and pumped directly into water wells. Closed systems generally are used where brine is to be injected into a formation other than the oil-producing formation, as a waste-disposal method.

2. Scale deposition: Crystals from the concentrated salt solutions tend to accumulate in pipelines and at the face of the formation. They restrict the flow of brine and increase pumping costs. Such scale deposits are controlled by the addition of chemicals, principally phosphates, to the brine at the injection-pump manifold.

3. Corrosion: Brines containing dissolved oxygen are very corrosive to ferrous metals. The phosphates added to prevent scale deposition act also as mild corrosion inhibitors, and usually no other corrosion-inhibiting chemicals are added to the brines. However, the corrosiveness of some brines, such as those containing carbonates, may be so great that corrosion inhibitors must be added to prevent loss of surface pipes.

### Inorganic Industrial Wastes

Analyses of the inorganic wastes of 18 companies are listed in Table 2 to illustrate the wide variety of chemical-process waste mixtures and to show the stark differences between these wastes and oilfield brines. These wastes have been classified as essentially neutral, basic, or acidic. The neutral wastes, which are low in dissolved organic compounds, are more similar in chemical behavior to oilfield brines than are the others.

The only preinjection treatment required for many of these neutral salt solutions is filtration. However, wastes containing dissolved organic compounds usually complicate underground injection by forming polymeric gums at the formation face and in pores near the well bore.

TABLE 2.--Inorganic wastes that are being injected into deep geologic formations

No.	Description of waste	Injec- tion rate, gpm	Injec- tion pres- sure, psi	Depth of Well, ft	Description of formation
Neutral Wastes					
1.	NH <sub>4</sub> Cl (15,000 ppm); NaCl (1,600 ppm); CaSO <sub>4</sub> (260 ppm); Na <sub>2</sub> CrO <sub>4</sub> (40 ppm); ZnCl <sub>2</sub> (5 ppm); urea (4,000 ppm)	900	200	900	Limestone - vugular
2.	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (32%); NaCl (1.5%); nitriles (0.07%); BOD = 10,000 ppm; pH = 6.7	1,000	500	7,000	Sandstone, 700' thick, $\phi$ = 28%; k = 300 md
3.	Na <sub>2</sub> SO <sub>4</sub> (800 ppm); NaCl (300 ppm); NaF (20 ppm); NaNO <sub>3</sub> (3 ppm); FeCl <sub>3</sub> (2 ppm); MnSO <sub>4</sub> (2 ppm); ZnCl <sub>2</sub> (5 ppm); phenols (500 ppm); detergents (300 ppm); pH 7.9, BOD = 50 ppm	50	0	3,000	Limestone - vugular
4.	Na <sub>2</sub> SO <sub>4</sub> (2,000 ppm); Na <sub>3</sub> PO <sub>4</sub> (10 ppm); FeCl <sub>3</sub> (800 ppm); NaNO <sub>3</sub> (100 ppm); Na <sub>2</sub> CrO <sub>4</sub> (10 ppm); pH = 7.5	80	0	3,800	Dolomite - vugular
5.	NaCl (1,800 ppm); CaCO <sub>3</sub> (400 ppm); MgCO <sub>3</sub> (400 ppm) (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (1,500 ppm); hydrocarbons (1,500 ppm); pH = 8.0	50	400	1,100	Unconsolidated sand; $\phi$ = 32%; k = 2,000 md
Basic Wastes					
6.	NaOH (3.0%); Na <sub>2</sub> SO <sub>4</sub> (1.0%); Phenol (1.0%); acetone (0.2%); pH = 12	100	300	6,500	Sandstone with beds of sand, gravel and clay. k = 200-1,000 md, $\phi$ = 28-32%.
7.	NaOH (7.5%); Na <sub>2</sub> S (1.2%); Na <sub>2</sub> CO <sub>3</sub> (2.2%); Na <sub>2</sub> SO <sub>4</sub> (0.7%); NaCl (0.3%); Phenols (0.5%); mercaptans (0.4%); pH = 9.4; BOD = 5,000 ppm	350	400	6,950	Unconsolidated sand, 250' thick
8.	NaOH (1.5%); Na <sub>2</sub> CO <sub>3</sub> (5.4%); NaCl (13.1%); Glycerine (5.0%); Epichlorohydrin (4.6%); Epoxy resin (1.9%); Phenol (3.2%); acetone (1.6%); pH = 11.2	150	200	6,200	Sandstone with beds of sand, gravel and clay. k = 200-1,000 md, $\phi$ = 28-32%.

TABLE 2.--Inorganic wastes that are being injected into deep geologic formations (cont.)

Injection rate, gpm	Injection pressure, psi	Depth of well, ft	Description of formation	Years in operation
1,100	1,000	5,800	Limestone, vugular, with sand inclusion in some areas. $\phi = 18\%$ , $k = 5$ md.	6
<p>95 ppm); NaCl (9,100 ppm); <math>\text{CaSO}_4</math> (1,500 ppm); <math>\text{MgSO}_4</math> (1,500 ppm); <math>\text{NH}_3</math> (1,500 ppm); adipic acid (1,500 ppm); organics (1,000 ppm); pH = 8.5. 1 (6.0%) and <math>\text{HNO}_3</math> (4.0%) are added in injection pump manifold.</p>				
50	150	4,300	Unconsolidated sand	2
200	100	7,200	Unconsolidated sands containing shale and clay; $\phi = 27$ ; $k = 1,000$ md	3
100	300	3,800	Unconsolidated sand alternating with shale, 1,500' thick, $\phi = 20\%$ , $k = 1,200$ md.	2
100	50	4,200	Unconsolidated sand, containing clay and shale, $k = 1,500$ md, $\phi = 32\%$	1
350	100	4,500	Unconsolidated sand, 800' thick, $\phi = 32$ ; $k = 1,500$ md	2
<p>4 (0.2%); <math>\text{H}_2\text{SO}_4</math> (0.2%); <math>\text{HNO}_3</math> (50 ppm) acids (50 ppm); Nitriles (100 ppm),</p>				
30	750	3,700	Sandstone containing chalk. $k = 10$ -1,000 md, $\phi = 20$ -25%	3
150	0	2,300	Sandstone, $\phi = 12\%$ , $k = 100$ md	6
150	0	2,300	Sandstone, $\phi = 12\%$ , $k = 100$ md	6
200	0	4,000	Limestone, vugular	12
<p>3%); <math>\text{Na}_2\text{SO}_4</math> (27.7%); <math>\text{H}_2\text{SO}_4</math> (7.8%); <math>\text{HCl}</math> (2.7%); Organic acids (4.7%); <math>\text{Oxg}</math>. (3.3%); alcohols (1.9%); ketones (1.1%) %; <math>\text{FeCl}_2</math> (23.4%) %; <math>\text{FeSO}_4</math> (13.0%) %; <math>\text{H}_2\text{SO}_4</math> (2.0%); NaCl (10%); acetic (1.0%); chloroacetic acid (1.0%); ate hydrocarbons (0.5%)</p>				

TABLE 3.--Organic wastes that are being injected into  
deep geologic formations

No.	Description of waste	Injec- tion rate, gpm	Injec- tion pres- sure, psi	Depth of Well, ft	Description of formation
	<u>Aldehydes</u>				
1.	Chlorinated aldehydes (1.9%); acetic acid (1.3%); acetaldehyde (0.3%); pH = 5	200	500	5,400	Unconsolidated sands ranging in thickness ft, separated by thin shale beds; $\phi = 30$
2.	Formaldehyde (0.4%); acetaldehyde (0.4%); Butyraldehyde (0.3%); crotonaldehyde (0.2%); methyl alcohol (0.2%); butyl alcohol (0.14%); acrolein (0.02%); formic acid (0.01%); acetic acid (0.01%)	850	600	4,500	Unconsolidated sand; $\phi = 30$ -40%; k = 1.0-
3.	Acetaldehyde (750 ppm); propanol (100 ppm); acetone (350 ppm); acrolein (100 ppm); butanol (150 ppm); methyl ethyl ketone (300 ppm); vinyl methanol ketone (600 ppm); cyclobutanone (600 ppm); dioxane (100 ppm); NaCl (5,000 ppm); NaHCO <sub>3</sub> (1,000 ppm); pH = 7.3	800	0	4,000	Sandstone and detrital granite; $\phi = 25$ %;
4.	<u>Alcohols</u> Hexanol (0.10%); amyl alcohol (0.06%); methanol (0.02%); dibasic acids (0.82%); hexamethylene imine (0.14%); cyclohexane (0.02%); dodecane (0.01%); NaNO <sub>3</sub> (1.3%); NaHCO <sub>3</sub> (0.35%); unidentified organics (2.40%); pH = 9.1	250	450	3,300	Loosely consolidated sand, 260 ft thick. k = 1.0 - 2.0 Darcy.
5.	Polyvinyl alcohol (300 ppm); methanol (1,400 ppm); acetic acid (400 ppm); hydroquinone (100); silicofones (23 ppm); vinyl acetate, (1,200 ppm); methyl acetate (800 ppm); acetaldehyde (500 ppm); ethyl acetate (50 ppm); sodium acetate (2,300 ppm); pH = 5	250	500	7,000	Sandstone interbedded with shale.

TABLE 3.--Organic wastes that are being injected into deep geologic formations (cont.)

No.	Description of waste	Injec- tion rate, gpm	Injec- tion pres- sure, psi	Depth of Well, ft	Description of formation
	<u>Glycols</u>				
6.	Ethylene glycol (1.0%); K <sub>2</sub> CO <sub>3</sub> (1.0%)	350	350	5,000	Unconsolidated
7.	Ethylene glycol (500 ppm); propylene dichloride (125 ppm); propylene glycol (11,000 ppm); acetone (40 ppm); ethylene dichloride (1,200 ppm); dichloroisopropyl ether (90 ppm); dichloroethyl ether (40 ppm); NaCl (5%); Na <sub>2</sub> SO <sub>4</sub> (0.05%); Na <sub>2</sub> CO <sub>3</sub> (0.01%)	300	300	6,000	Unconsolidated sand.
	<u>Phenols</u>				
8.	Phenols (6.2%); cyanides (1.2%); ammonia (0.3%); thiocyanides (0.1%); NaCl (0.3%)	100	0	1,800	Sandstone, k = 200 md. Ø = 15%
	<u>Acids</u>				
9.	Acetic acid (0.5%); chloroacetic acid (0.4%); acetaldehyde (0.1%); acetaldehyde (0.1%); Butanol (0.05%); crotonaldehyde (0.05%); NaCl (0.5%); pH = 2.5, COD = 29, 400 ppm; BOD = 9,900 ppm.	350	400	3,500	Unconsolidated sand. Ø = 27-35%; k = 0
10.	Adipic acid (8%); caprolactam (1%); butanol (0.5%); benzene (0.2%); cyclohexane (0.3%); NaCl (2%)	100	350	6,000	Sandstone, k = 0.2-1.0 Darcy, Ø = 28%
11.	Organic acids (dibasic - principally adipic) (2.6%); nitric acid (0.8%)	400	200	5,200	Loosely consolidated sand.
12.	Acetic acid (3,000 ppm); paratoluic acid (100 ppm); benzoic acid (50 ppm); xylene (100 ppm); methyl ethyl ketone (50 ppm); CaCl <sub>2</sub> (200 ppm); MgSO <sub>4</sub> (200 ppm); pH = 3.0	200	400	6,000	Sandstone, Ø = 30%; k = 500 md

TABLE 3.--Organic wastes that are being injected into deep geologic formations (cont.)

No.	Description of waste	Injec- tion rate, gpm	Injec- tion pres- sure, psi	Depth of Well, ft	Description of formation
13.	C <sub>2</sub> -C <sub>6</sub> organic acids (6,700 ppm); C <sub>1</sub> -C <sub>4</sub> alcohols (2,000 ppm); C <sub>1</sub> -C <sub>3</sub> ketones (1,400 ppm); propylene glycols (400 ppm); propyl esters (2,000 ppm); propylene oxide (3,000 ppm); C <sub>5</sub> -C <sub>6</sub> hydrocarbon (2,000 ppm); Na <sub>2</sub> SO <sub>4</sub> (2,000 ppm); NaCl (500 ppm)	400	800	7,000	Sandstone; $\phi = 27\%$ ; $k = 300$ md.
14.	Acetic acid (160 ppm); maleic acid (100 ppm); xylene sulfonic acid (50 ppm); benzoic acid (50 ppm); butyl alcohol (950 ppm); styrene (100 ppm); isopropanol (100 ppm); phthalic acid (300 ppm); methyl ethyl ketone (250 ppm); NaOH (650 ppm); H <sub>2</sub> SO <sub>4</sub> (500 ppm); Na <sub>2</sub> CO <sub>3</sub> (350 ppm)	250	1,200	7,200	Sandstone containing beds of clay; $k = 200$
15.	<u>Nitriles</u> Glycol nitrile (0.5%); iminodiacetonitrile (0.3%); nitrilotriacetoneitrile (0.2%); other organic nitriles (1.0%); methanol (0.1%); methyl formate (0.1%); formaldehyde (0.3%); formic acid (0.5%); H <sub>2</sub> SO <sub>4</sub> (1.7%); (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> (4.3%)	150	200	6,500	Sandstone, 400 ft thick, $\phi = 28\%$ ; $k = 200$
16.	<u>Disulfides</u> Ethyl disulfide (30%); propyl disulfide (40%); butyl disulfide (25%); mercaptans (5%); water insoluble oil	5	0	2,200	Unconsolidated sand with thin clay beds, 1
17.	Ethyl disulfide (4%); propyl disulfide (6%); butyl disulfide (14%); pentyl disulfide (14%); hexyl disulfide (3%); NaOH (8%)	10	60	1,500	Vugular limestone

disposal of oilfield brines. Pore spaces near the well bore can quickly become plugged. Insoluble salts of metals in the waste can be deposited in the pores, or hydroxides of metals may form gels that effectively plug the pores. Resinlike materials, such as the epoxy resin in Waste 8 (Table 2), may polymerize in the formation and plug the pores.

Waste mixtures may also react with clay minerals such as montmorillonite and illite (14), found in most sedimentary rocks, causing the clay to swell and reducing the permeability of the formation. This problem is especially troublesome with dilute neutral wastes. Reactions of components in the waste with formation brine or constituents of the formation matrix may cause the evolution of gas, which can produce high pressures and loss of permeability near the well bore.

Where the degree of incompatibility between the formation brine and waste is high, a large volume (200,000 to 500,000 gal) of a nonreactive fluid can be injected ahead of the waste to act as a buffer between the two incompatible fluids. The degree of mixing in the formation between the injected fluid and native brine is relatively small. Mixing occurs in a thin transient zone, and its rate, quantity, and adverse effects depend on the chemical and physical properties of the native brine, the formation, and the wastes. It is only when this mixing occurs in or near the well bore that severe problems arise. The nonreactive buffering fluid injected in front of the waste moves the mixing zone in the formation far away from the well bore so that incompatibility is no longer an adverse factor.

Because inorganic acidic wastes are highly corrosive, they present additional problems of acceptability for underground injection. Corrosion of surface equipment and well components can cause plugging of the formation from the insoluble reaction products. If corrosion can be minimized and initial incompatibility problems eliminated by developing a buffer zone of nonreactive fluid, the injection of low-pH wastes proceeds with ease, regardless of the type of formation selected for injection.

As injection proceeds, the permeability of the formation gradually increases. This fact was demonstrated with rock core samples in the laboratory experiments of Champlin and co-workers (4). They injected a simulated acidic waste into several outcrop cores and examined the physical properties of the sandstone cores before and after injection of the acidic solutions. In every



loosely bound with cementing materials, and (3) degradation of particles such as clay.

The success that the steel companies are having with the injection of waste pickle liquor (2) into the Mount Simon Sandstone is a good practical example of the injection of highly corrosive acidic wastes. Wastes 16 and 17 of Table 2 are two types of waste pickle-liquor hydrochloric and sulfuric acid, respectively. They contain a high load of iron that amounts to as much as 20 tons/day when injected at the current average rates. The wells disposing of these acidic wastes have been in operation for more than 15 years.

Acidic wastes are also being successfully injected into limestone and dolomite formations (6,7,8). Reactions of these acids with the carbonate formations have not caused adverse permeability problems, perhaps because the carbon dioxide formed by the reaction is sufficiently soluble in the waste and formation brines to be removed from the vicinity of the well bore by the fluid entering the formation.

#### Organic Industrial Wastes

The analyses of 15 waste mixtures that are aqueous solutions of organic waste constituents, many of which contain dissolved inorganic salts, are divided in Table 3 into categories that are most descriptive of the mixtures. The disulfide wastes (16 and 17 of Table 3) are water-insoluble oils that are being injected successfully without any attempt to make them water soluble.

The aldehydes, phenols, and nitriles have in common a marked tendency to form water-insoluble gums at the face of the disposal formation. Wells injecting such wastes must be stimulated periodically. Acidizing with a mixture of hydrochloric and hydrofluoric acids is the most common treatment, but it commonly is necessary to remove well tubing and reenter the well with drilling tools to remove the accumulation of gum from the formation face. Hydraulic fracturing, induced by pumping liquid in at high pressure until the strata are ruptured, is also employed for stimulation of wells completed in consolidated sandstone or carbonate rock.

The only other troublesome wastes listed in Table 3 are those containing low-boiling-point components that are irritants to the skin and mucous membranes, or are toxic. Wastes 2 and 3 contain acrolein, and Waste 9 contains chloroacetic acid; both

## SURFACE EQUIPMENT

Aqueous fluids scheduled for injection into subsurface strata must be free of suspended solids, oil, and gas. The solids create a restriction to flow at the face of the formation, commonly called the "skin effect," and the oil and gas decrease the permeability to the aqueous phase by competing for the flow channels. Therefore, the objective of preinjection treatment of wastes is to remove solids, oil, and gas, or to stabilize a waste that may have a tendency to form a second phase during injection.

The selection of surface equipment depends on the physical and chemical properties of the waste and on the reservoir characteristics of the formation that has been selected for storage. The least complex systems are those designed to process wastes that are noncorrosive and free of suspended solids. The surface equipment required to process this waste includes: (1) a collecting tank; (2) transfer pipes; (3) an injection pump, if surface pressure is required for injection at the maximum flow rate of the waste; and (4) controls, such as float valves and recorders. There are a few such simple installations, but they are not typical because most industrial wastes cannot be injected into subsurface formations without previous treatment at the surface.

Waste from a chemical plant is generally a mixture of several waste streams from separate manufacturing units, cooling-tower blowdown, laboratory sinks, etc. Hence, the waste-disposal system begins with a sewer line that delivers the waste composite to a collecting reservoir or sump. The simplest sump is a cement sump placed several feet below the surface to allow gravity drainage. If the sump has a retention time of less than 1 hour, sedimentation of suspended solids will not occur to a large degree, and only an occasional raking of the sediment will be required. If a longer retention time is required in the sump, an automatic raking device usually must be installed to prevent sludge accumulation.

Waste-collecting ponds up to 2 million gallons in capacity and lined with an impermeable material may be used. Such large ponds are used to provide a long retention time and also to allow for mixing of the wastes by convection. Hence, these ponds are used where the wastes comprise several waste streams of different composition. A great disadvantage to large ponds with long retention times is the growth of bacteria and algae.

be removed by coagulation and sedimentation. Some wastes contain too much suspended solids for economical filtration, and the solids will not settle in sedimentation tanks without the aid of coagulants. Coagulants are also used where the disposal formation has very small pores, because the pores will be plugged by fine suspended solids that cannot be removed efficiently by filtration.

The size and type of injection pump to be installed are governed by the wellhead pressure, the volume of fluid, and the necessary rate of injection at peak loads. A few installations do not require an injection pump because the hydrostatic pressure of the column of waste in the disposal well exerts sufficient pressure at the subsurface face of the formation to inject the waste. If the wellhead pressure for waste injection is less than 150 psi, simple single-stage centrifugal pumps can be used; but, at higher pressure, multiplex piston-type or multistage centrifugal pumps are needed. Hence, selection of an injection pump must be delayed until the disposal well is ready for operation, and pumping tests can be made.

Some requirements for surface equipment and pretreatment of waste can be determined by testing the waste and the water of the disposal formation. Results of such tests will indicate the compatibility of the formation water and waste, and are useful in determining the treatment required. Even though compatibility can be determined in the laboratory, conditions as they exist underground are difficult to duplicate. A laboratory mixture of the two fluids that apparently is satisfactory may be incompatible in the subsurface, or the opposite may be true. Bernard (3) made some studies by pumping water solutions into sandstone samples that contained incompatible interstitial solutions. He did not observe a decrease in permeability that would have indicated plugging.

Because of the diverse nature of chemical wastes and disposal formations, the surface equipment for a waste-injection system cannot be designed until the formation to be used has been examined. The wastes from chemical manufacturing operations also vary greatly in chemical and physical properties. Therefore, each injection system is unique because the surface equipment is designed to process a specific waste for injection into a specific local portion of a formation. The best way to discuss surface equipment is to cite several examples, ranging from the simplest to the most complex. Three examples selected from the lists of wastes in Tables 2 and 3 are used to illustrate the variety in design and operation of surface equipment.

waste is of Table 2. The waste is a mixture containing hydrochloric acid as a major constituent. However, the waste mixture is not complicated with suspended solids or undissolved oils that would have to be removed before injection. In addition, initial injectivity tests showed that the geologic conditions permitted the waste to be injected into the disposal formation, a vugular limestone at a depth of 4,000 ft (1,220 m), at the maximum anticipated flow rate under gravity flow. No injection pump was needed to force the waste into the formation, and the absence of suspended solids eliminated the need for filtration. Only a collecting sump and a metering valve to control the flow of waste into the well were required.

A 6-in., steel-jacketed, polyethylene pipe transports the waste from the control valve to the wellhead, and the fluid pressure in this pipe is monitored. A light oil is maintained under pressure in the annulus of the well to support the fiber-cast tubing and to detect tubing leaks. A break in the tubing will cause an immediate change of pressure in the annulus.

The flow rate (averaged over a 30-day period) is 200 gpm with a slight vacuum at the wellhead and 35 psi pressure in the annulus. The average temperature of the waste at the wellhead is 120° F. Flow rates fluctuate from 450 gpm, which is in excess of the capacity of the well during periods of heavy rainfall, to a minimum of 110 gpm.

#### Closed System

A more complex system designed to process Waste 9 of Table 3 is illustrated in Figure 2. The waste is a water solution, very low in pH, containing hydrochloric acid, acetic acid, chloroacetaldehydes, and chloroacetic acids. Although the organic concentration of the waste generally does not exceed 3% the low-boiling chlorinated hydrocarbon compounds make this a very reactive solution which is extremely irritating to mucous membranes and to skin. Therefore, this waste is handled in a completely closed system.

The selection of materials for construction of the surface equipment was a critical design consideration, because the waste is extremely corrosive to standard construction materials. Epoxy plastic pipe, Hastelloy C, 316 stainless steel, and titanium are used as required.

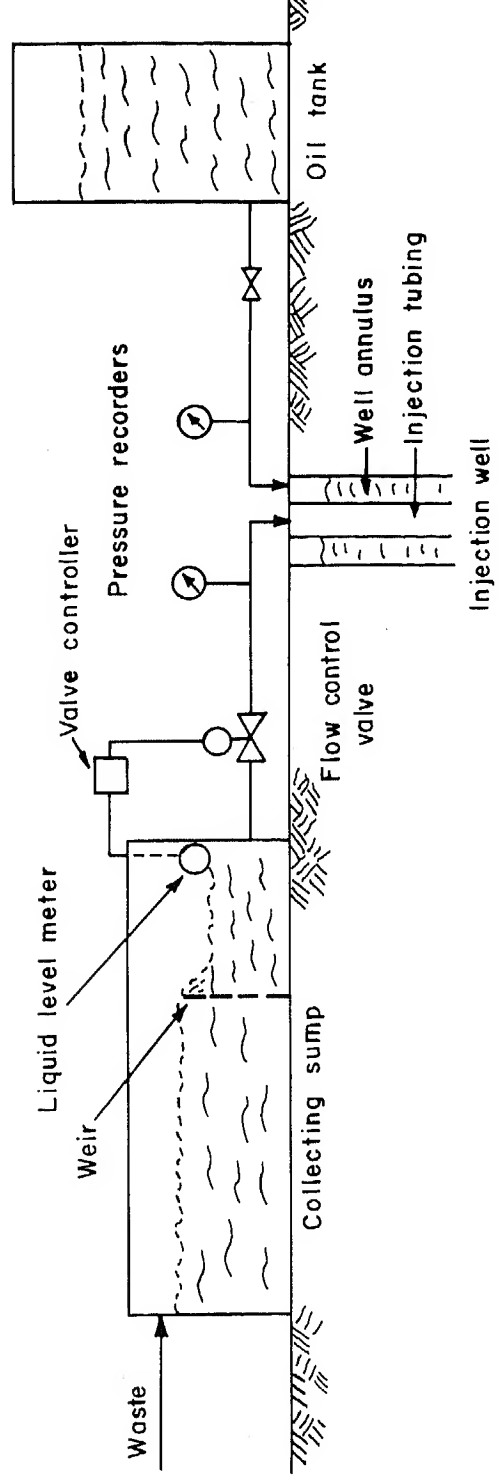


FIGURE 1.- Open Surface Equipment Used in One of the Simplest Waste-Injection Systems.

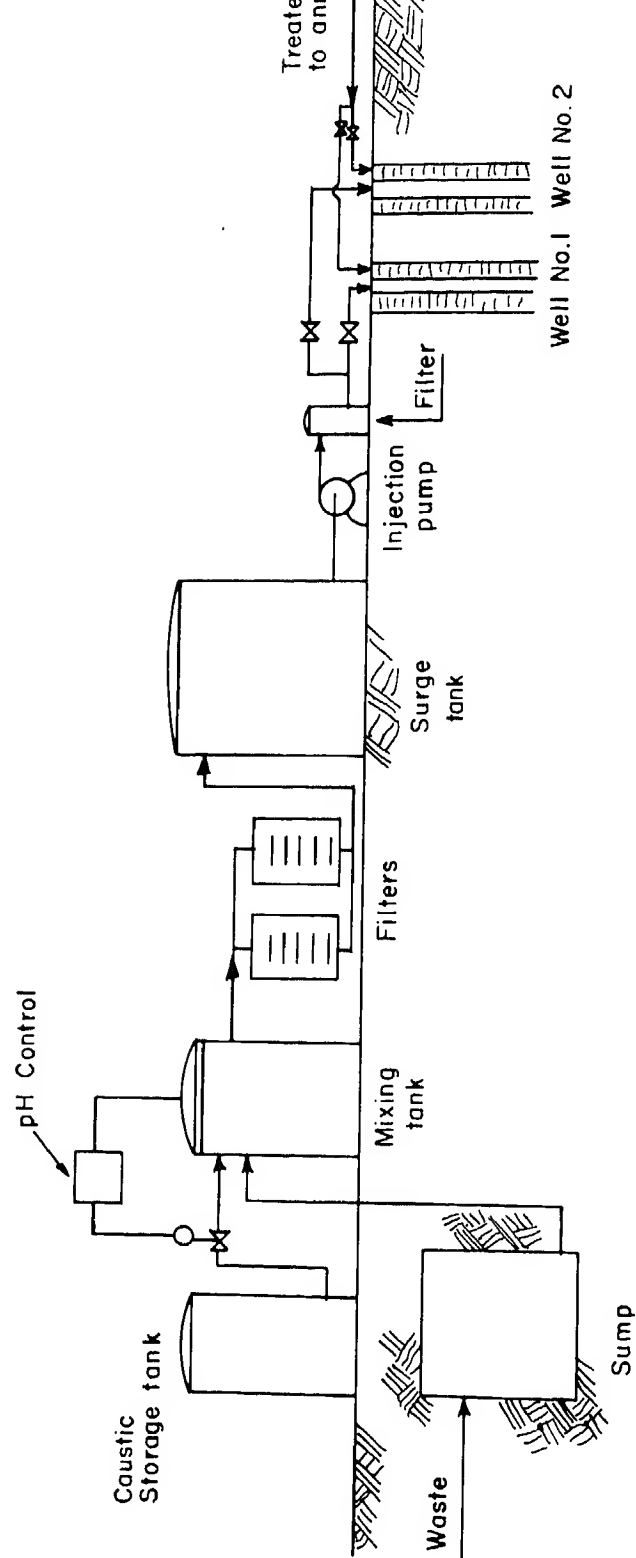


FIGURE 2.— Closed Surface Equipment Used for Wastes Containing Volatile Organic Components.

polymers that precipitate upon standing, and, at a pH greater than 5.0, a tarlike polymer is formed by aldol condensation of the aldehydes.

Following pH control, the waste is filtered in rack-type pressure filters that are designed for backwash and precoat operation as completely closed systems. The processed waste is stored in a surge tank equipped with a liquid-level meter that controls the operation of the injection pump. As a final precaution, just prior to injection into one of the two wells, the waste is passed through a cartridge filter to remove any suspended solids that may have accumulated or formed during retention in the surge tank.

Two wells are maintained because the plant operation is completely dependent on the continued injection of the waste. There are no other provisions for disposal of this waste; hence, if only one injection well were used, failure of the well to receive the waste because of injection-tubing breakage, plugging, or other problems would result in complete shutdown of the chemical plant and considerable economic loss.

The annulus between the injection casing and the tubing is filled with boiler feed water which is reduced in pressure from 800 to 300 psi. The pressure of this fluid in the annulus is monitored continuously as a means of detecting tubing or packer leaks. Two single-stage centrifugal pumps connected in series are used to inject the waste at an average 350-gpm flow rate and 400 psi wellhead pressure.

#### Complex Open System

One of the most complex of the industrial waste-disposal systems is illustrated in Figure 3. It was designed to process Waste 9 of Table 2 for injection into a "tight" limestone. The waste contains a large load of suspended solids and some oil as it enters the collecting pond. The oil is skimmed from the surface with an automatic skimmer that travels slowly across the pond. The skimmed oil is burned in an incinerator. The waste then is treated with coagulators to accelerate sedimentation of the suspended solids, and with waste hydrochloric acid for pH control.

The sludge from the coagulator and backwash from the filters are sent to a drying bed, and the underdrain is returned to the collecting pond. A series of four leaf filters is used to filter the effluent from the coagulator, and the waste then is stored in

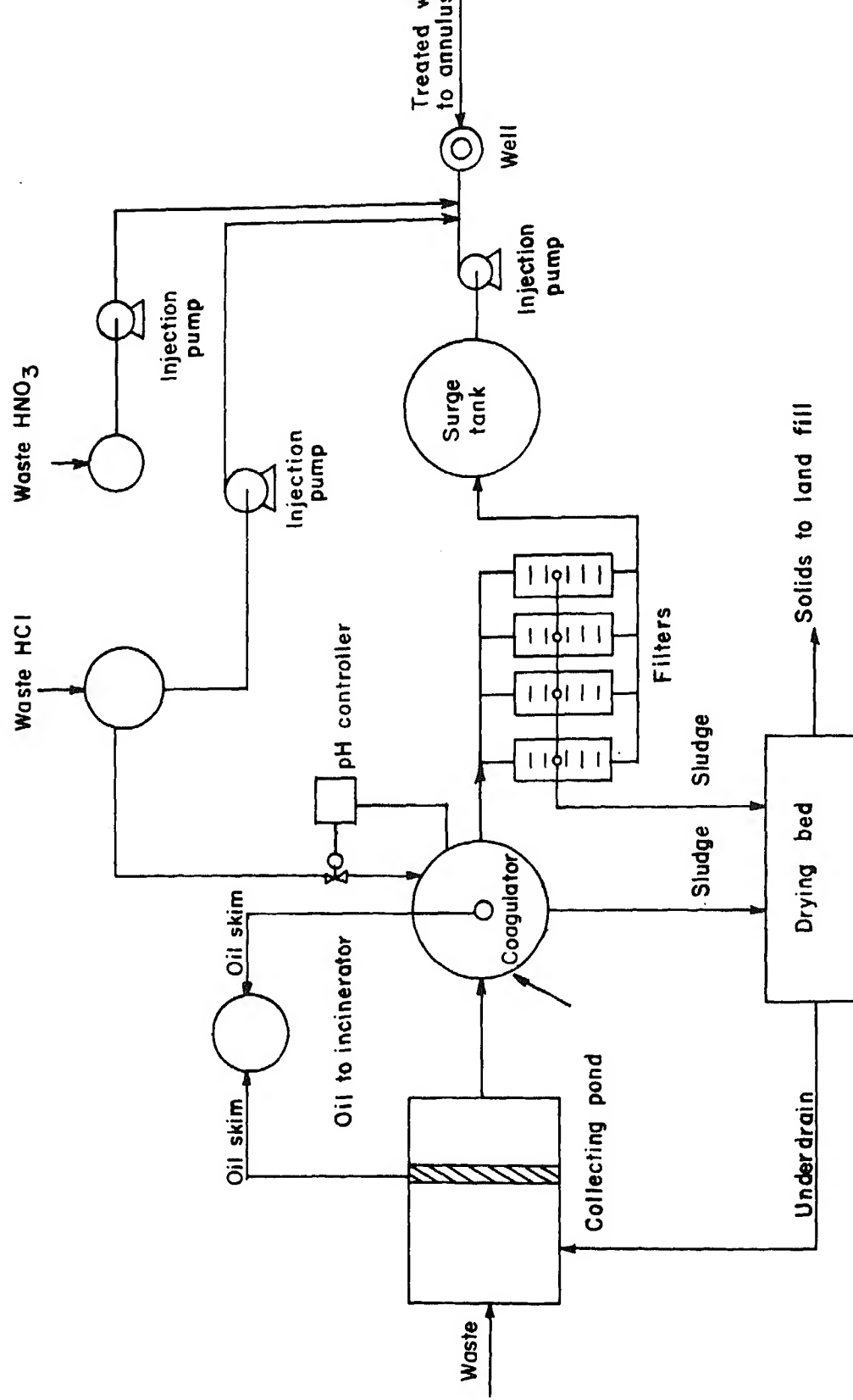


FIGURE 3.-Complex Open Waste Injection System.



streams are collected in separate tanks and pumped into the injection-pump manifold. The waste acids are collected separately because the waste streams are not constant; therefore, if the acids were added directly to the collecting pond, they would cause wide variations in the pH of the composite waste.

## WASTE-INJECTION WELL DESIGN

### Drilling and Casing

One of the most important criteria of a waste-disposal well is that it must be designed for complete protection of the near-surface, low-salinity aquifers through which the well is drilled. To accomplish such protection, a 12- to 18-in.-diameter hole is drilled to a depth at least 200 ft (60 m) below the deepest freshwater aquifer encountered. Surface casing (Fig. 4), at least 2 in. smaller than the hole diameter and equipped with centralizers, is run to the bottom of the hole. The annular space between the casing and the well bore is filled with cement. Experience with brine-injection wells has shown that this procedure will protect the freshwater aquifers from contamination if the injection casing is damaged.

After the surface casing has been installed, drilling is continued with an 8- to 12-in.-diameter bit through the potential disposal formations. Core samples of the potential disposal zones should be taken for laboratory examination, and the hole should be logged.

When a suitable disposal formation is selected, a 6- to 9-in.-OD string of casing - the injection casing - is centered in the hole, and cement is circulated to the surface in the annulus between the casing and the well bore (Fig. 4). The well is completed in the disposal zone by one of many methods, depending on the nature of the formation and the waste intended for disposal. Three of the most commonly used completion methods are illustrated in Figure 5.

### Well Completion

If the formation is friable, indicating that the well bore may tend to cave and fill the bottom of the hole, a cased-hole completion technique (Fig. 5A) is used to provide positive support for the well-bore walls. For this type of completion, the hole is drilled to the bottom of the disposal formation, casing is set, and cement is circulated to the surface. The

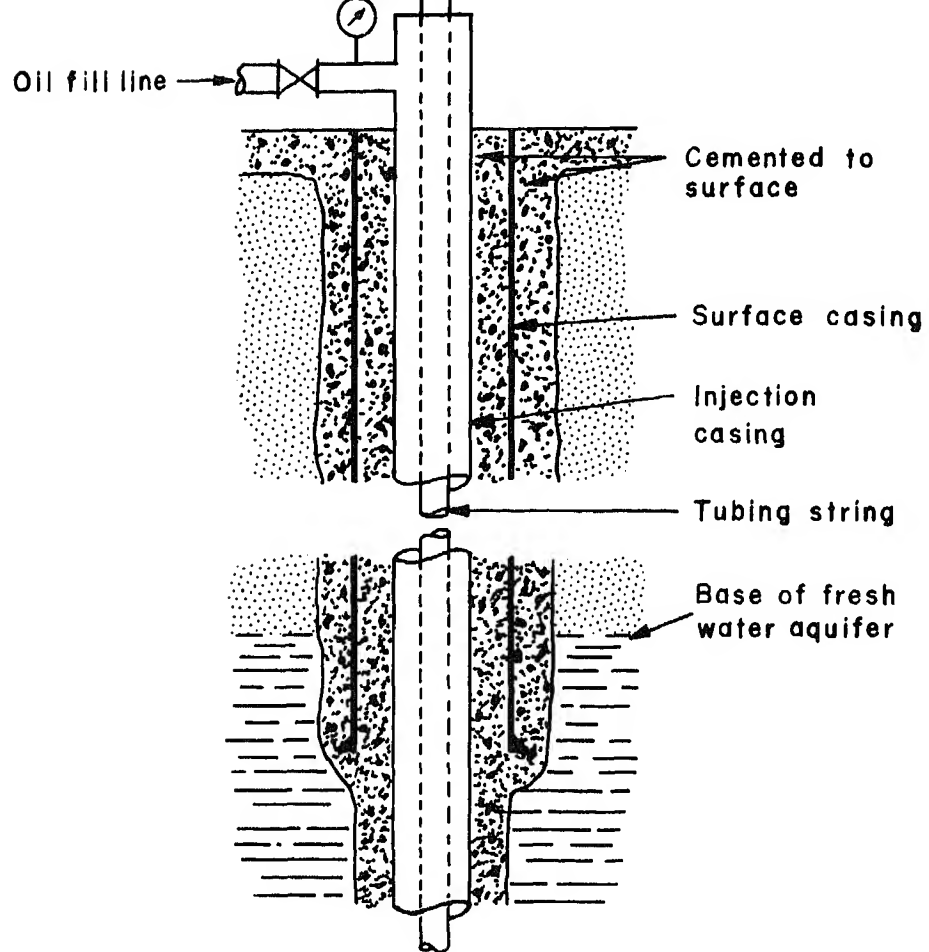


FIGURE 4.-Waste-Disposal Well .

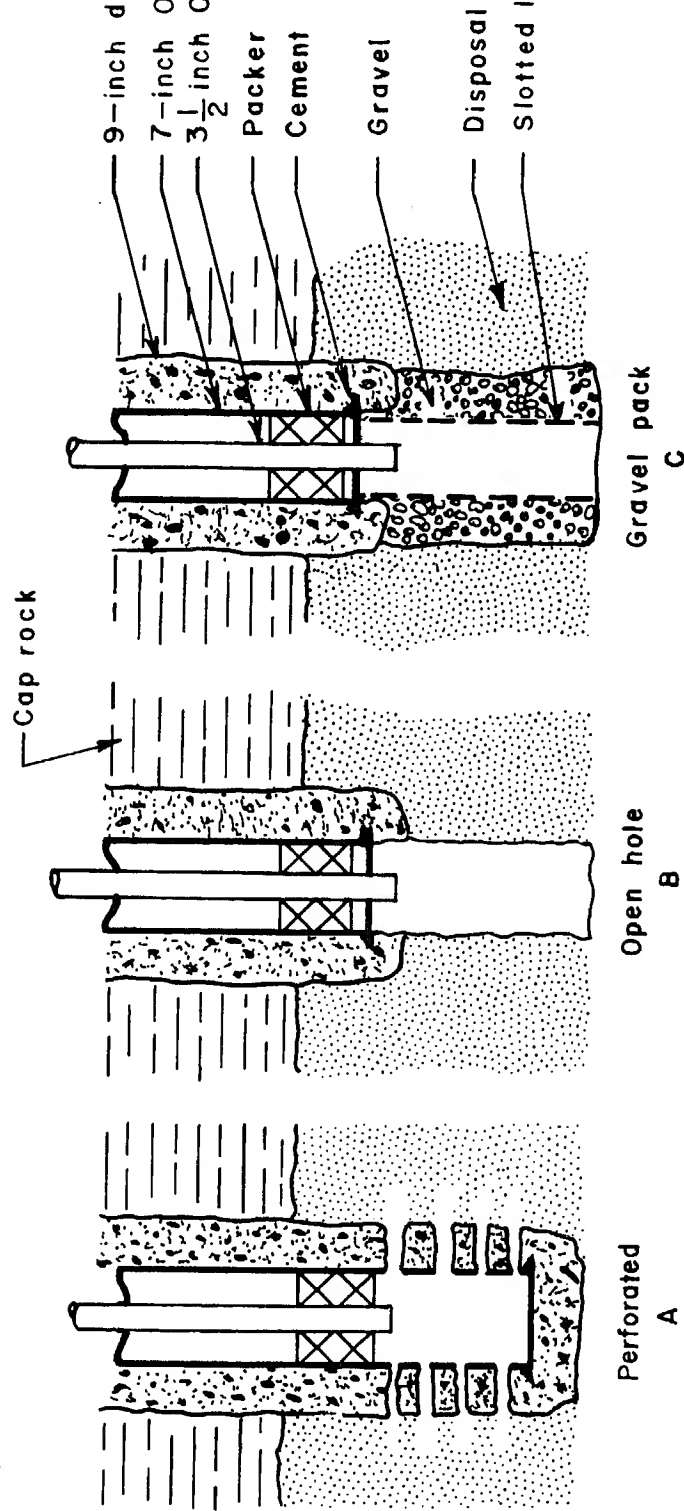


FIGURE 5.- Disposal-Well Completion Methods .

zone, should be constructed of material such as stainless steel.

Where the disposal zone is a hard consolidated sandstone or a vugular carbonate formation, open-hole completion (Fig. 5B) may be used. Casing is set at the top of the disposal formation and cemented to the surface. Then an open hole is drilled to the bottom of the disposal zone. Open-hole completion also is used if corrosive wastes are to be injected, because products from corrosion of the casing in the disposal zone may plug the formation. Corrosion will also cause casing adjacent to the disposal zone to fail, allowing the cement to crumble and fill the hole with debris.

The third general type of completion, gravel pack (Fig. 5C), is used in unconsolidated sands to prevent sand from filling the bottom section of the injection casing or tubing, and thereby restricting the flow of the waste solution. The sand and gravel pack together at the bottom of the casing to form a tortuous path for the sand moving toward the well casing. The formation sand jams and movement stops; however, space for unrestricted liquid flow is left between the grains of sand and gravel.

Several other completion methods are used in unconsolidated sand. If the well is less than 2,000 ft (600 m) deep, air-lift valves may be installed in the annulus between the casing and tubing. Whenever sand restricts the flow of waste, the bottom section of casing can be cleaned of sand by blowing air through the tubing to lift the sand through the annulus. Another method is to perforate the casing with 1/10-in.-diameter pinholes adjacent to the sand formation (10). The sand may also be consolidated by treatment with epoxy plastic (11).

Sometimes the waste is injected directly through the injection casing, but this practice is inadvisable for corrosive waste, even with plastic-coated pipe, since absence of pinholes in the plastic coating cannot be guaranteed. The injection casing is best protected by use of an injection-tubing string inside the casing. Although some tubing strings made of corrosion-resistant metal alloys are used, the most popular material is a fiberglass-epoxy tubing, because of its high resistance to corrosive materials and its light weight.

Usually a packer is installed at the bottom of the long string of tubing in the annulus between the casing and tubing (Fig. 5). Additional protection of the injection casing is

tubing.

A special type of completion is used in some of the wells designed for injection of waste steel-pickling liquor (Wastes 16 and 17, Table 2). A packer is not used at the bottom of the tubing to seal the annular space between the tubing and casing, as illustrated in Figure 5B; instead, electrodes are installed at the bottom of the tubing in the annular space. Water is pumped continuously into the annulus at a pressure slightly greater than the pressure of the waste in the tubing, allowing a constant flow of water through the annular space. The conductivity of water at the bottom of the tubing is monitored to detect accidental entry of acid into the annular space.

This brief discussion of well construction and completion is included only to show the principal features of design. A more complete presentation of the details of construction and procedures used in the construction of waste-disposal wells was given by Baker (1).

### FORMATION CHARACTERISTICS

A subsurface-disposal system can be successful only if a porous, permeable formation of wide areal extent is available at sufficient depth to insure safety for storage and retention of the injected fluids. The stratum must be below all freshwater aquifers and confined vertically by rocks that, for practical purposes, are impermeable to waste liquids. In addition to the protection of usable water resources, the vertical confinement of liquid wastes also protects any developed or undeveloped hydrocarbon and mineral deposits.

Rocks that comprise the earth's crust are classified as igneous, metamorphic, and sedimentary. Of these, sedimentary rocks, particularly those that were deposited in a marine environment, are most likely to have good injection characteristics. Under favorable circumstances, however, both igneous and metamorphic rocks can have sufficient porosity and permeability to receive large volumes of liquid.

Some of the more suitable sedimentary rocks are sandstone, limestone, and dolomite. These rocks usually are porous and permeable enough to be used as injection zones. Naturally fractured limestones, dolomites, and shales may provide satisfactory injection horizons. However, the kind of rock most favorable for industrial waste disposal depends upon the chemical nature of the specific waste to be injected and should be determined for each disposal project.

adequate containment and monitoring of injected fluids.

The injection zone must be isolated, both above and below, to prevent the vertical escape of injected waste. Unfractured shale, clay, slate, anhydrite, gypsum, marl, and bentonite have been found by the petroleum industry to provide good seals against the upward flow of oil and gas (13). The formation thickness required to confine liquid industrial waste cannot be rigidly established. A confining stratum only 10 or 20 ft thick may provide a satisfactory seal to retain oil and gas. However, the risk would be too great to use beds of this thickness to confine industrial wastes because the formation would be very susceptible to fracturing during waste injection and also could contain thin natural fractures as shown in Figure 6.

Sedimentary rocks originally were deposited in uniform layers at the bottom of ancient seas; however, some were later uplifted, folded, and faulted by forces in the earth's crust into anticlinal (positive) and synclinal (negative) structures as shown by Figure 7. Oil and gas often occur in anticlinal folds because they are less dense than water and seek a position of lowest fluid potential. Hence, it is probable that injected waste with a density less than that of interstitial water would tend to remain trapped in a closed anticlinal structure (Fig. 7A), whereas waste with a density greater than interstitial water would tend to remain in a closed synclinal structure (Fig. 7B).

Faults, defined by Lahee (12) as a failure along which there has been slippage of the contiguous masses against each other, offset strata and place them in contact with other older or younger beds of the same or different rock types, as shown in Figure 8. Fractured formations should not be considered for confining or disposal of wastes.

Other geologic configurations suitable for the confinement of limited volumes of liquid waste, depending on their areal extent, are sandstone lenses with both vertical and horizontal confining beds (Fig. 9) and stratigraphic traps (Fig. 10).

In addition to stratigraphy, structure, and rock properties, aquifer hydrodynamics may be significant in the evaluation of waste-injection well sites. The presence of a natural hydrodynamic gradient in the injection zone will cause the injected waste to be distributed asymmetrically around the wellbore and transported through the aquifer even after injection has ceased. Several aspects of the subsurface movement of natural fluids or injected wastes under a hydrodynamic gradient are discussed by Young and Galley (15).

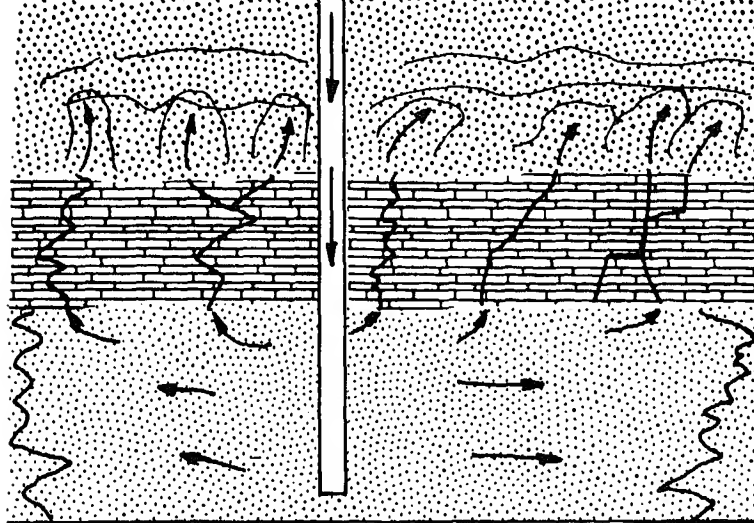
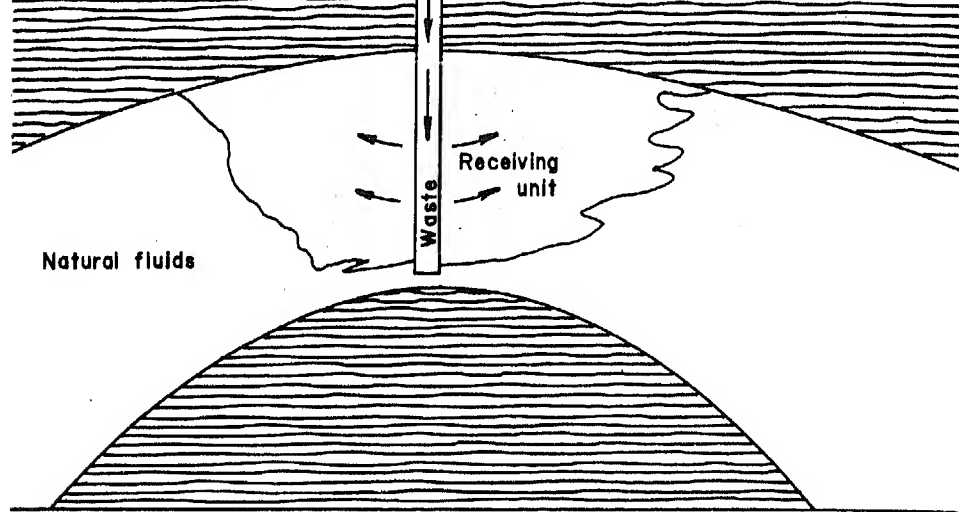
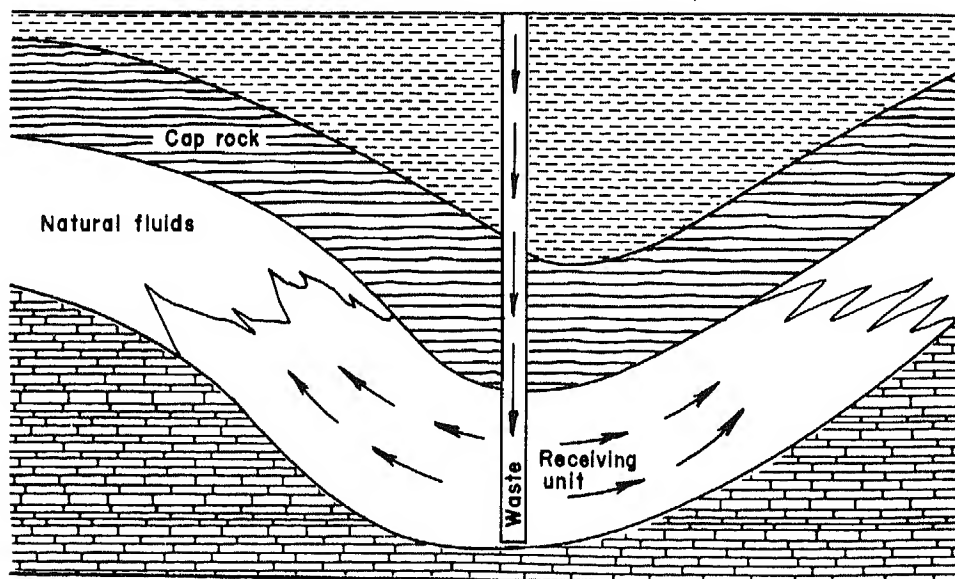


FIGURE 6 :Fluid Migrating Upward  
Through a Fractured Confining  
Formation.



A. - Anticlinal structure with injected liquid waste less dense than interstitial water.



B. - Synclinal structure with injected liquid waste denser than interstitial water.

FIGURE 7 .- Configurations From Folded Sedimentary Rocks.



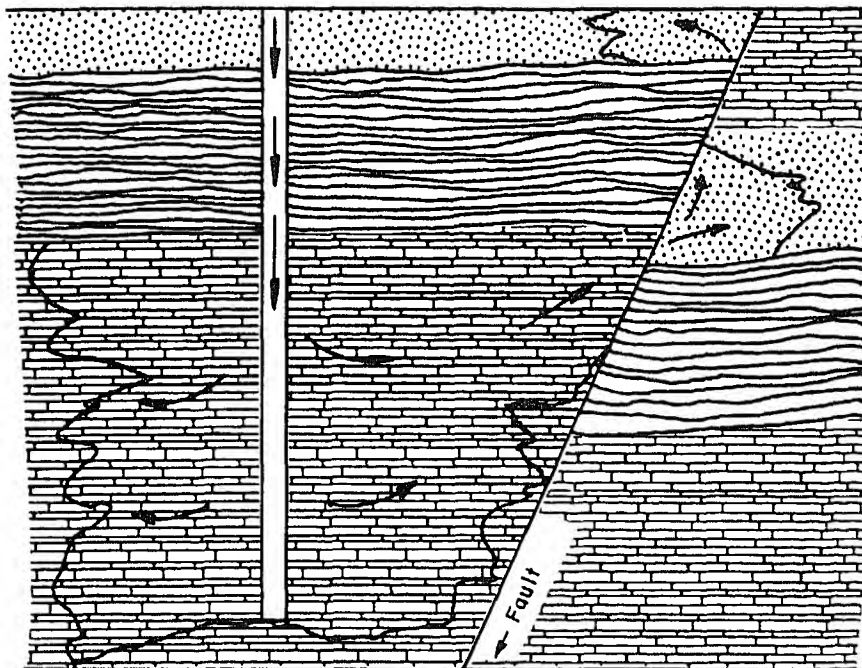


FIGURE 8 .-Faulted Formation Showing How Injected Fluid Could be Lost to Another Formation.

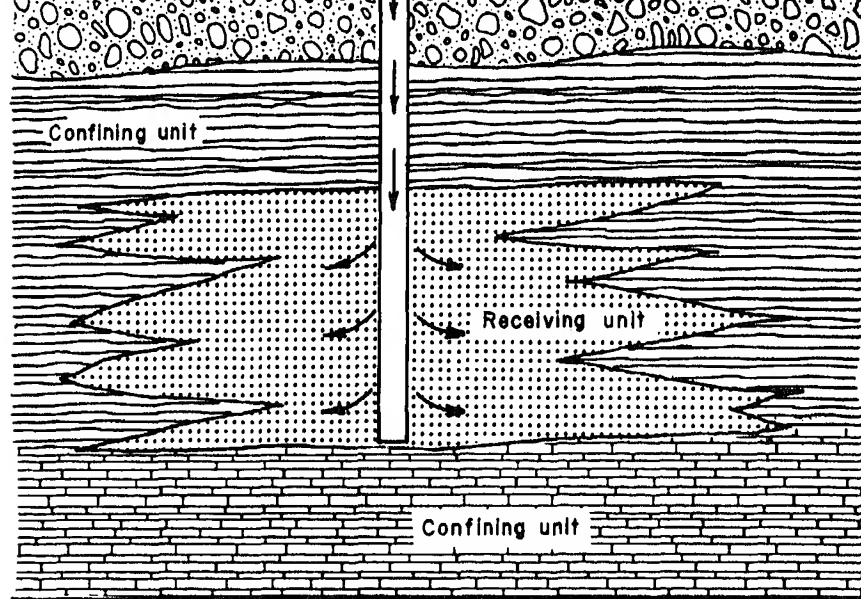


FIGURE 9 .- Sandstone Lens With Horizontal and Vertical Confining Formations.

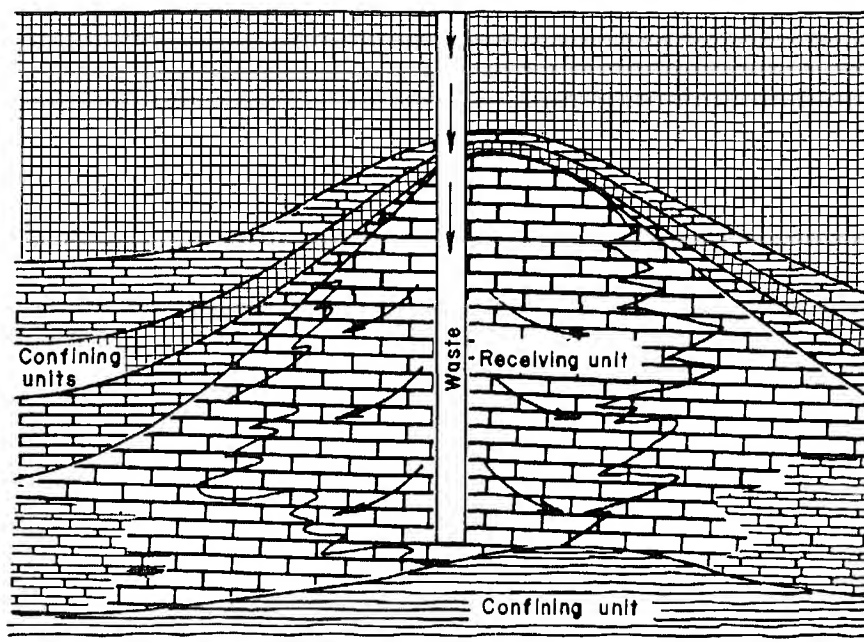


FIGURE 10 .- Stratigraphic Trap

posal system will depend on the amount of space available for waste storage by compression of the interstitial fluids (gas and brine) and the rock matrix. The reservoir pressure will gradually build to a point where continued injection would be inadvisable because of possible fracturing of the confining strata. However, of the disposal installations that were studied in detail (6), no limitations of fluid injection were experienced as a result of excessive pressure caused by fluid confinement.

Sandstone, vugular carbonate (limestone and dolomite) formations, and unconsolidated sand are the three general lithologic types that are currently being used for injection of industrial wastes.

The permeability and porosity of unconsolidated sand units cannot be determined accurately in a laboratory. These properties vary with the degree and method of compaction, and it is impossible to duplicate the subsurface conditions in a small laboratory sample.

Some consolidated sandstone formations are quite homogeneous over wide areas; thus, laboratory analyses of permeability and porosity of cores taken throughout the thickness of the formation are very useful in well completion and analysis of problems that develop later in the life of the well. The Mount Simon Formation near Gary, Indiana, is being used for injection of waste steel-pickling acids, such as Wastes 16 and 17 of Table 2. The average porosity of 14.7% and permeability of 456 md are fairly consistent throughout the range in depth.

Vugular carbonate formations are difficult to evaluate in the laboratory because the vugs are so diverse in size and shape, ranging from microscopic pinholes to vugs the diameter of a pencil. The best method of evaluation is through pumping tests after well completion.

#### HISTORY OF AN INJECTION SYSTEM

Source and Nature of the Waste: When the plant was put into operation in 1962, two large holding ponds were constructed in an attempt to contain and evaporate the waste generated in the plant. One of these ponds was unsuccessfully used as an algae stabilization pond in an attempt to control the BOD such that the waste might be disposed of into a nearby river. Because of lack of significant solar evaporation in the area, these ponds remained

that were under free cultivation.

Prior to 1965, the manufacturing facilities were confined to the production of acetaldehyde, butanol, and other organic compounds by cracking natural gas. The waste from these operations consisted of cooling-tower and boiler-water waste containing about 1.1 wt% organic compounds (Table 4). This waste is injected into Well 1, which was completed in July 1964, at a rate between 417,000 and 576,000 gal/day.

In 1965, the plant was expanded, particularly the acetaldehyde program, and hexamethylenediamine and vinyl acetate are additional products that were included during expansion of the plant. The volume of waste from the new units (Table 5) varies from 36,000 to 280,000 gal/day. Since April 1965, this waste has been injected into a second well located 1,200 ft from the first well (9).

Geology: The wells are located near the Gulf Coast of Texas. The area is characterized by the outcrop of the Beaumont Clay. Recent alluvial deposits border the Colorado River and some of its tributaries. Immediately underlying the Beaumont Clay is the Lissie Formation, which extends to a depth of approximately 1,300 ft. These Pleistocene rocks consist predominately of sand and sandstone with intercalated shale and clay and overlie an undetermined thickness (greater than 11,000 ft) of largely undifferentiated sand, sandstone, and shale of Tertiary age. These Gulf Coast formations strike generally east-northeast and dip toward the southeast at approximately 30 ft/mile.

The interval chosen to receive the fluid waste is a well-developed persistent thick sand bed of considerable areal extent. It occurs at a depth of approximately 3,400 ft and is about 250 ft thick over several miles. Electric logs of oil exploration tests in the area indicate it to be predominantly well-sorted, fine-grained sand containing highly saline water. The interval is not productive of hydrocarbons in the region, the shallowest oil and gas production in the area being from the Frio sand at approximately 10,000 ft.

Surface Equipment: The two waste streams are treated separately, but in a similar manner. The waste from the various processes is accumulated in the process waste sump, which is a cement pit constructed low enough in the ground to take advantage of gravity drainage from the units. The composite waste is pumped from the sump to a settler-skimmer where oil and sediments are removed.

Organic constituents, ppm:	
Acetaldehyde.....	1,000
Acetaldol.....	900
Acetic acid.....	5,000
Butanol-1.....	1,300
Butyraldehyde.....	1,100
Chloroacetaldehyde.....	800
Crotonaldehyde.....	400
Phenol.....	1,200
Propionic acid.....	2,200
Inorganic constituents, ppm:	
Calcium.....	100
Iron.....	10
Magnesium.....	50
Sodium.....	3,000
Chloride.....	2,000
Sulfate.....	100
General Properties:	
Total hardness.....ppm..	350
Conductance.....micromhos..	10,000
pH.....	5
Temperature.....° F..	160

TABLE 5. - Composition of waste injected into well 2,

(Color: pale yellow, cloudy; odor: stale fish)

Organic constituents, ppm:	
Ammonia.....	500
Amyl alcohol.....	600
Cyclohexane.....	200
Dodecane.....	100
Hexanol.....	1,000
1-Hexylamine.....	1,400
1,2-Hexylamine.....	300
Methanol.....	200
Valeric acid.....	900
Inorganic constituents, ppm:	
Ammonium nitrate.....	4,000
Sodium bicarbonate.....	3,000
Sodium carbonate.....	600
Sodium nitrate.....	6,000
Sodium nitrite.....	7,000
Copper.....	80
Vanadium.....	20
Manganese.....	50
General properties:	
pH.....	9
Temperature.....° F..	120

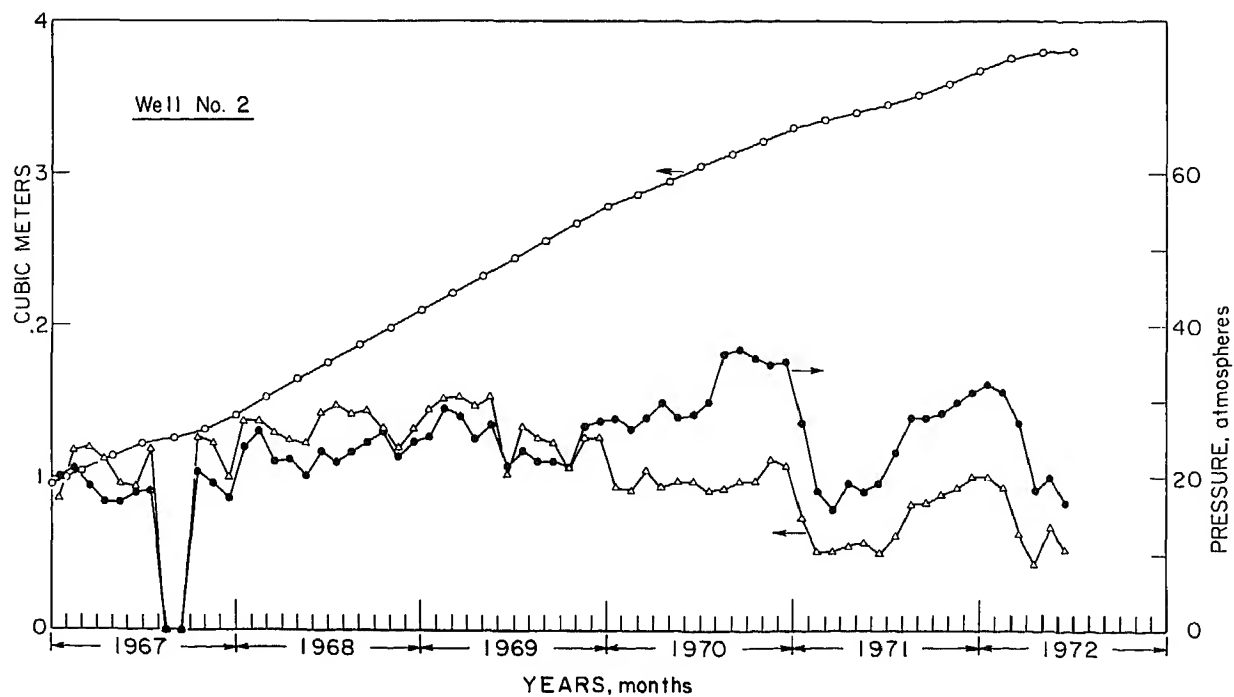
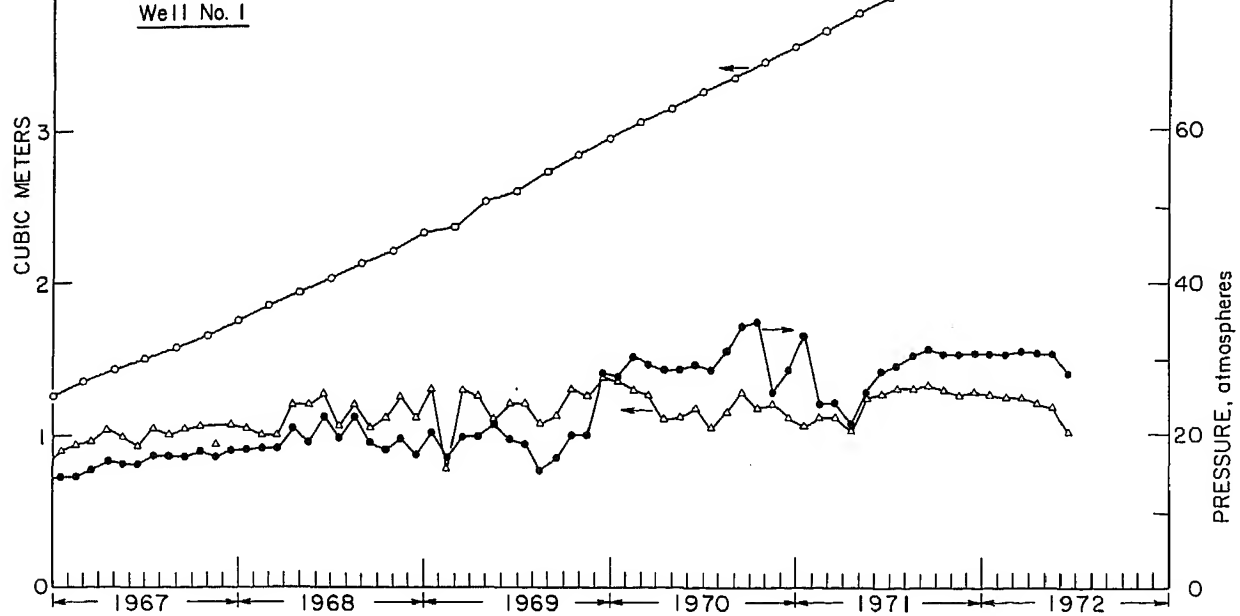


FIGURE 11. - Operating Histories of Two Injection Wells.

filtration in two stages: (1) removal of the major portion of the suspended solids with a leaf filter using diatomaceous earth precoat, and (2) final filtration with cartridge-type high-pressure filters.

Two centrifugal pumps are used as needed to inject the waste from a surge tank into Well 1. Waste 2 is pumped from the setter-skimmer through two cartridge-type filters to a surge tank. Two centrifugal pumps are used as needed to inject the waste into Well 2.

Well Completion and Operation: The surface casing of the first well consists of 10 3/4-in J-55 pipe set at a depth of 1,500 ft and cemented to the surface to protect freshwater bearing sands. A string of 7-in J-55 casing is set from the surface to the bottom of the well at 3,750 ft and cemented in with a special acid-resistant cement. The injection string is 4 1/2-in fiberglass tubing that is also cemented with the special acid-resistant cement. When this tubing was installed, the joints were made up with epoxy resin to insure a good seal. Perforations were made through both casings from 3,400 to 3,600 ft. Injection was started in November 1964.

Well 2 is 2,750 ft from Well 1. The surface string in Well 2 is 13 3/8-in H-40 casing set at 1,400 ft and cemented to the surface to protect the freshwater-bearing sands. A string of 9 5/8-in J-55 casing is set from the surface to the bottom of the hole at 3,750 ft and cemented in place. This casing is perforated from 3,500 to 3,600 ft. Injection into this well was started in April 1965.

Figures 11A and 11B show the well injection histories of Wells 1 and 2, respectively. The average monthly volumes injected and wellhead pressures remained in synchronization with no abnormalities until November 1969, when an obvious increase in the wellhead pressure of both wells occurred. This is undoubtedly due to mutual interference between the wells that began in November 1969 and became progressively more pronounced as injection of fluid continued.

## CONCLUSIONS

It is apparent that injection of liquid wastes into deep geologic formations can solve many difficult waste-disposal problems. However, limitations of the knowledge of how the waste



consideration in the planning stages.

The chemical and physical interactions of the waste constituents with the geologic materials at the temperatures and pressures that prevail in the subsurface environment are unknown. However, there is some evidence to indicate that adsorption and chemical reaction will retard the advance of waste constituents away from the well bore. Instead of complete volumetric displacement, the waste constituents are probably stratified behind an advancing liquid front of water containing dissolved salts not too dissimilar from the native formation brine. Accurate predictions of the migration patterns of waste constituents cannot be made until the adsorption, chemical reaction, and ion-exchange properties of each component of the waste mixture are known.

An accurate estimate of the total cost of a proposed waste-injection system can be made only when complete analyses of the waste, geologic formation, and native brine are available. A thorough evaluation of the waste must be made with respect to suspended solids, ranges of pH that promote precipitation, and chemical compatibility with the underground brine. The formation must be studied to determine the porosity, permeability, thickness, areal extent, lithology, and pore-size distribution. When these analyses are obtained, the design and cost estimate of the surface equipment and injection well can be made.

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**SESSION 12**

**FOSSIL FUEL POWER GENERATION – ADVANCED METHODS (GASIFICATION).**

**Chairman: Ralph Scott**

**Co-Chairman: G. L. Wiesenfeld**



Oak Ridge National Laboratory

Data on the treatment of aqueous coal conversion waste are needed to ensure that water supply and quality are not adversely affected by the developing coal conversion industry. This work is not intended to develop new wastewater treatment processes, but to provide useful and timely information on the application of known control technologies to coal conversion wastewaters.

Samples of lignitic coal and steam-plant fly ash have been tested for their ability to remove polyaromatic hydrocarbons (PAHs) and refractory phenolics from aqueous streams. Removal of up to 99% of the organics was obtained with solid loadings as high as 15 mg/g. In experiments with a tapered fluidized-bed bioreactor, phenol reductions of  $\sim 99.9\%$  were achieved at phenol degradation rates of 7 to 10 kg per day per  $m^3$  of reactor volume. Ozonation tests have shown that, with biologically treated wastewater, 99% of the residual phenol and 22 to 97% of the refractory PAHs, along with most of the associated colors and odors, can be degraded using ozone dosages of 0.01 to 0.14 kg per thousand liters. Experiments using wet oxidation for the destruction of both soluble and absorbed organics have been initiated. (Research sponsored by the Division of Environmental Control Technology, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.)

CONTROL ASPECTS OF UNDERGROUND COAL GASIFICATION

- a. Preliminary Environmental Results of the LETC Hanna III  
Underground Coal Gasification Experiment

Joseph E. Virgona, Theodore C. Bartke, and John E. Boysen  
U.S. Department of Energy  
Laramie Energy Technology Center

- b. LLL Investigations of Ground-Water and Subsidence Effects\*

S. Warren Mead, Francis T. Wang, and Harold C. Ganow  
Lawrence Livermore Laboratory

Changes in ground-water quality and the possible effects of subsidence and ground movement induced by the underground gasification cavity represent significant environmental concerns associated with underground coal gasification (UCG). Parallel environmental studies are being conducted by the Laramie Energy Technology Center (LETC) and the Lawrence Livermore Laboratory (LLL) near Hanna and Gillette, Wyoming, respectively, to characterize these

terminated.

Their first paper (Part I) discusses the LETC Hanna III environmental studies. The Hanna III experiment (June-July, 1977) was designed primarily to provide information on the potential impacts of UCG on ground-water quality and the environmental control technology implications of those impacts. In addition, parameters critical to the process itself were examined. Preliminary results of the ground-water monitoring during the pre-operational, operational, and early portion of the post-operational phases will be presented.

The second paper (Part II) covers ground-water and subsidence measurements carried out at the sites of two in situ coal gasification experiments conducted in northeastern Wyoming by LLL. Ground-water measurements and complementary laboratory studies have helped to clarify the environmental significance of reaction-product contaminants that remain underground following gasification. Extensive roof collapse into the gasification cavity has been documented by subsurface geotechnical measurements.

\*Support for these investigations is provided by the Division of Environmental Control Technology (DOE/ASEV), the Office of Research and Development (EPA/IERL-CI), and the Division of Fossil Fuel Extraction (DOE/ASET). This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore Laboratory under contract number W-7405-ENG-48.

#### ANALYTICAL STUDY OF THE EFFLUENTS FROM A HIGH-TEMPERATURE ENTRAINED FLOW COAL GASIFIER

L. D. Hansen, L. R. Phillips, R. B. Ahlgren, N. F. Mangelson,  
D. J. Eatough, and M. L. Lee

Brigham Young University

Effluent streams from a 100 pound per hour, pressurized, high temperature, entrained flow coal gasifier have been found to be extremely clean compared to those of other gasifiers. The water-scrubbed gaseous effluent contained only CO, H<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, and traces of H<sub>2</sub>S and HCN. The gas obtained by depressurization of the scrubber water contained trace amounts of SO<sub>2</sub> in addition to these other seven gases. Polycyclic aromatic hydrocarbons, the only non-volatile organic compounds found in the scrubber water,

cerns. Statistical analysis was used to determine the effects of the process parameters: coal type, coal feed rate, reactor pressure, oxygen to coal ration, and stream to coal ratio.

Sufficient environmental control can be achieved by removing the  $H_2S$  from the gaseous effluent using an appropriate commercial process and by separating the particulate matter from the scrubber water. Particulate matter separation methods include flocculation settling, froth flotation and filtration. Flocculation is probably the most economical of these separation methods. Laboratory bench scale separation tests and mass balance calculations should provide valuable information as to which environmental control technology is most economically feasible.

## CLEANING PRODUCER GAS FROM THE METC GASIFIER

A.S. Moore, K. Pater, C. Ray, and R.J. Belt

U.S. Department of Energy  
Morgantown Energy Technology Center

### ABSTRACT

The Morgantown Energy Technology Center (METC) of the Department of Energy is developing a system to clean Low-Btu gas made from coal. The gas is generated in a prototype pressurized stirred fixed-bed gas producer developed in earlier work at METC that gasifies 909 Kg/hr (1 tph) of caking bituminous coal. The objective is to clean the gas to the degree needed both by any end-use system consuming the gas, and to ensure that effluents from the end-use system meet emission requirement. This report described pilot-scale development of a prototype gas cleanup system using a sidestream portion of the full 4,248,000 lit/hr (150,000 scfh) gas output from the METC gas producer. A full-flow gas cleanup system, developed as a result of the sidestream pilot-scale test investigations, is being installed and tested in phases throughout 1978. Experience with particulate, tar, light oil, and alkali removal with the side stream scrubber and experience with particulate and tar removal in the developmental testing of the full stream scrubber are reviewed.

Quench water is a principal wastewater from coal conversion processes that employ wet cleaning of gasses. The origin of the water is moisture in the coal and steam injected into the coal conversion reactor. Depending upon coal composition the quench water contains chlorides, flourides, ammonia, hydrogen sulfide and sulfur oxides. With tar producing coal conversion technology the quench water also contains cyanides, thiocyanates, phenols and various organics.

A two stage gas quenching process was proposed to absorb strong electrolytes in a small flow first-stage quench so as to improve the feasibility of reuse of the larger volume second-stage quench. A study was made to compare the technical and economic feasibility of two-stage quenching with conventional single-stage quenching.

The study evaluated methodology for estimation of quench water characteristics and engineered a concept for accomplishment of the two-stage quench. The results indicated that strong electrolytes could be absorbed from the gasses to a high degree in a first-stage quench with a blowdown of from 5 to 10 percent of the total condensate. The blowdown would be purged to waste disposal. The second-stage quench would collect 90-95 percent of the condensate containing a low content of strong electrolytes. The condensate containing weak electrolytes and organics would be treated by steam stripping and bioxidation prior to reuse as process water. Alternative disposal concepts were evaluated for two sites using representative Eastern and Western coals.

ENVIRONMENTAL CONTROL ACTIVITIES ON  
SLAGGING FIXED-BED GASIFICATION AT THE  
GRAND FORKS ENERGY TECHNOLOGY CENTER

R. C. Ellman, E. A. Sondreal  
U.S. Department of Energy  
Grand Forks Energy Technology Center

The 25-TPD pilot SFBG at the GFETC was reactivated in 1976 for the purpose of supporting the development and commercialization of the slagging fixed-bed gasification process. A major objective was the development of a detailed environmental assessment, including characterization of both gaseous and liquid effluents. This assessment will substantially apply both to the Hi-Btu demonstration plant currently being designed based on SFBG technology and to fixed-bed, dry-ash Lurgi gasifiers planned for first generation SNG plants.



ment and application of sampling procedures and analytical methods for characterizing gaseous and liquid effluents; 3) studies on gas cooling, separation of tar and byproducts, and treatment of waste water; 4) studies on disposal of gasifier slag and other waste solids; 5) the relation of effluent properties to gasifier operating variables, and 6) assessment of biomedical effects due to tars and waste water constituents. This report will present a summary of the assessment plan and selected data on the characterization of gaseous and liquid effluents performed to date.

OVERVIEW OF THE SYNTHANE PILOT PLANT  
ENVIRONMENTAL ASSURANCE PROGRAM

by

R. P. Ladesic, R. L. Scott, and W. C. Peters  
U.S. Department of Energy  
Pittsburgh Energy Technology Center

An historical account of the development and current studies of environmental monitoring and compliance at the SYNTHANE pilot plant will be presented. This account will include the experiences and problems in establishing monitoring programs in the following areas:

Air:

Ambient Monitoring  
Stack Testing  
Fugitive Emissions

Noise:

Background  
In Plant

Water:

Surface Water Control  
NPDES Sampling  
Continuous Water Monitoring

Solid Waste:

Characterization  
Disposal

Occupation Health:

Problem and Direction

In February and March 1975 the first ambient air background studies were undertaken at the SYNTHANE pilot plant. Subsequent to these initial studies an environmental monitoring and compliance program was developed incorporating the areas noted above. The cost of this program to date plus facilities and equipment amount to approximately three (3) million dollars. The experience provided in interfacing with the technology development and developing the environmental monitoring and compliance program can be of value to all who are involved in small scale and large scale development.

## ABSTRACT

Data on the treatment of aqueous coal conversion waste are needed to ensure that water supply and quality are not adversely affected by the developing coal conversion industry. This work is not intended to develop new wastewater treatment processes but to provide useful and timely information on the application of known control technologies to coal conversion wastewaters.

Samples of lignitic coal and steam-plant fly ash have been tested for their ability to remove polynuclear aromatic hydrocarbons (PAHs) and refractory phenolics from aqueous streams. Removal of up to 99% of the organics was obtained. In experiments with a tapered fluidized-bed bioreactor, phenol reductions of ~99.9% were achieved at phenol degradation rates of 7 to 10 kg per day per m<sup>3</sup> of reactor volume. Ozonation tests have shown that, with biologically treated wastewater, 99% of the residual phenol and 22 to 97% of the refractory PAHs, along with most of the associated colors and odors, can be degraded using ozone dosages of <0.25 kg per thousand liters.

## 1. INTRODUCTION

The abundance of this country's coal resources, relative to those for crude oil and natural gas, has prompted both the Federal government and industry to undertake an intensive effort to develop processes for converting this solid form of energy into substitute gaseous and liquid fuels. Water is an essential raw material for these coal conversion processes. Process cooling is only one of the many reasons for this dependency. Often more than 30% of the energy in the coal feed is discarded as water vapor in the cooling towers. The impurities in the makeup water are discarded as wet sludges and/or blowdown streams heavily laden with contaminants. Water is also used as a source of the hydrogen needed to raise the atomic hydrogen-to-carbon ratio of coal from <1.0 to the approximate 1.5 to 3.5 values found in crude oil and natural gas, respectively. Depending on the hydrogen production process,

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\* Research sponsored by the Division of Environmental Control Technology, U.S. Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

it has been estimated that by the year 2000 wastewater discharges from all types of coal conversion facilities will total nearly 700 million tons/year.

Environmental and economic reasons will compel developers of coal conversion processes to maximize water reuse and to reduce pollutant levels in aqueous effluents. Because of the economic incentives favoring location of a coal conversion facility close to the mine mouth, water resources available to such a plant will be either relatively scarce and highly competed for by nonindustrial users such as farmers, municipalities, and recreationists (as in Colorado, Wyoming, Montana, North Dakota, and New Mexico), or they will be relatively abundant but heavily used by other industrial facilities (as in Kentucky, West Virginia, and Illinois). Environmental considerations aside, recovery of dissolved "pollutants" as process by-products (e.g., phenol) may become economically desirable because of raw material scarcities; however, it is difficult to justify at the present time, except for very large-scale conversion plants. Thus, ensuring the availability of adequate technology for treating the wastewaters from coal conversion processes may be as necessary a part of fostering the commercialization of a synthetic fuels industry as the development of the coal conversion technology itself.

Only recently has the development of the necessary control technology for the cleanup of coal wastewaters gained sufficient emphasis to consider its integration into the coal conversion implementation program. However, most control technology studies are considered to be add-ons for a particular coal conversion process. Unfortunately this viewpoint is often encouraged by the separation of those charged with the development of the technology from those investigating the technology available for the cleanup of aqueous streams. In many cases, judicious design of the various individual conversion process modules could allow minimal control modifications to clean up much of the wastewater problem. Given that the discharge of a wastewater stream is unavoidable, the determination of the amount of cleanup needed is a function of both present and future effluent regulations and of the proposed use of the effluent water. The development of these future regulations is presently causing a good deal of concern to those within EPA and to other investigators in the field.

## 2. COMPOSITION OF COAL CONVERSION WASTEWATER

Recent studies<sup>2-5</sup> of several coal gasification and liquefaction processes have identified the following operations as sources of wastewater: (1) separation of excess water from raw liquid products, (2) quenching and scrubbing of raw fuel gas, and (3) desulfurization and demetallization of raw liquid products. Other parts of the overall processes will provide additional sources of wastewater: (1) coal storage

Although wide variations exist in the composition of coal conversion wastewaters, generalizations can be formulated, depending on the type of process, operating conditions, and the nature of the coal used. The major constituents and concentrations of a representative wastewater are listed in Table 1.<sup>2</sup> The high phenol and ammonia concentrations are typical of coal conversion process wastewaters, whether they are condensation liquors or scrubber waters. Also listed are the concentration ranges expected in future Federal regulations for a variety of components. Standards for related industries such as coking and petroleum refining were used to develop these values<sup>2,6-7</sup> because there are as yet no regulations for the coal conversion industry. As shown, the levels of all the components listed will far exceed the limits of the anticipated regulations.

Individual variations do exist between the component concentrations of the various wastewaters. Although these variations are not shown, they may be quite important in the consideration of specific control technologies. The presence of a significant quantity of a metallic compound, for example, could alter the effectiveness of a biological or oxidative treatment system.

A survey of the literature reveals a number of presently available and proposed technologies for the cleanup of wastewaters with compositions similar to those indicated in Table 1.<sup>2</sup> As expected, they represent a wide range of removal efficiencies, final residual concentration levels, and costs. Efforts to obtain the relative economic costs of various environmental control technologies for the treatment of aqueous wastes from coal conversion processes have been completed.<sup>2</sup> Six processes have been identified as potentially promising in this area: ozonation, adsorption, biological degradation, solvent extraction, membrane processes, and coagulation-flocculation. The economic position of the various control technologies is shown in Fig. 1 where treatment costs are plotted versus residual organic levels.

### 3. ORNL'S WASTEWATER TREATMENT PROGRAM

ORNL's involvement in environmental control technology consists of an assessment and screening test evaluation of the amenability of coal hydrocarbonization wastewater and other coal conversion wastewaters to various treatment technologies. As part of this program, a flow sheet was proposed that takes advantage of several available unit operations and addresses the complete treatment of coal conversion wastewaters. This processing scheme is shown in Fig. 2 and includes physical, chemical, and biological treatment of the waste stream. The unit operations that are being investigated at ORNL include the bioreactor, the adsorption

Table 1. Composition of a typical coal conversion wastewater

Component	Concentration in wastewater ( $\mu\text{g}/\text{cm}^3$ )	Limits of anticipated regulations ( $\mu\text{g}/\text{cm}^3$ )
Phenol	6,000	0.03-0.3
NH <sub>3</sub>	10,000	0.8 -5.0
H <sub>2</sub> S	1,000	0.02-0.2
CN <sup>-</sup>	100	0.02-0.1
SCN <sup>-</sup>	500	
PAH	10	
TOC	20,000	BOD 4-30 COD 20-350

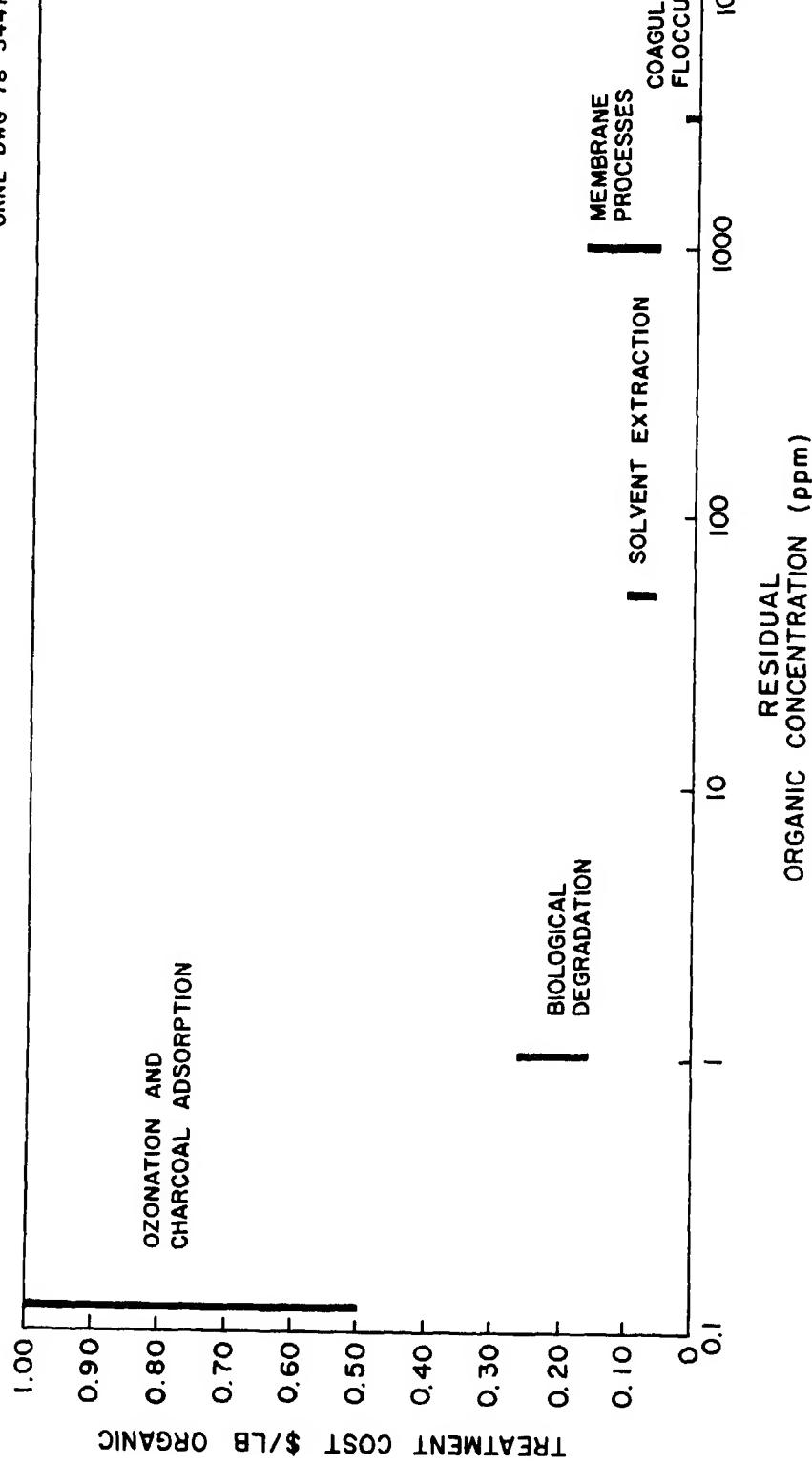


Fig. 1. Economic costs of environmental control technologies for aqueous coal conversion wastes.

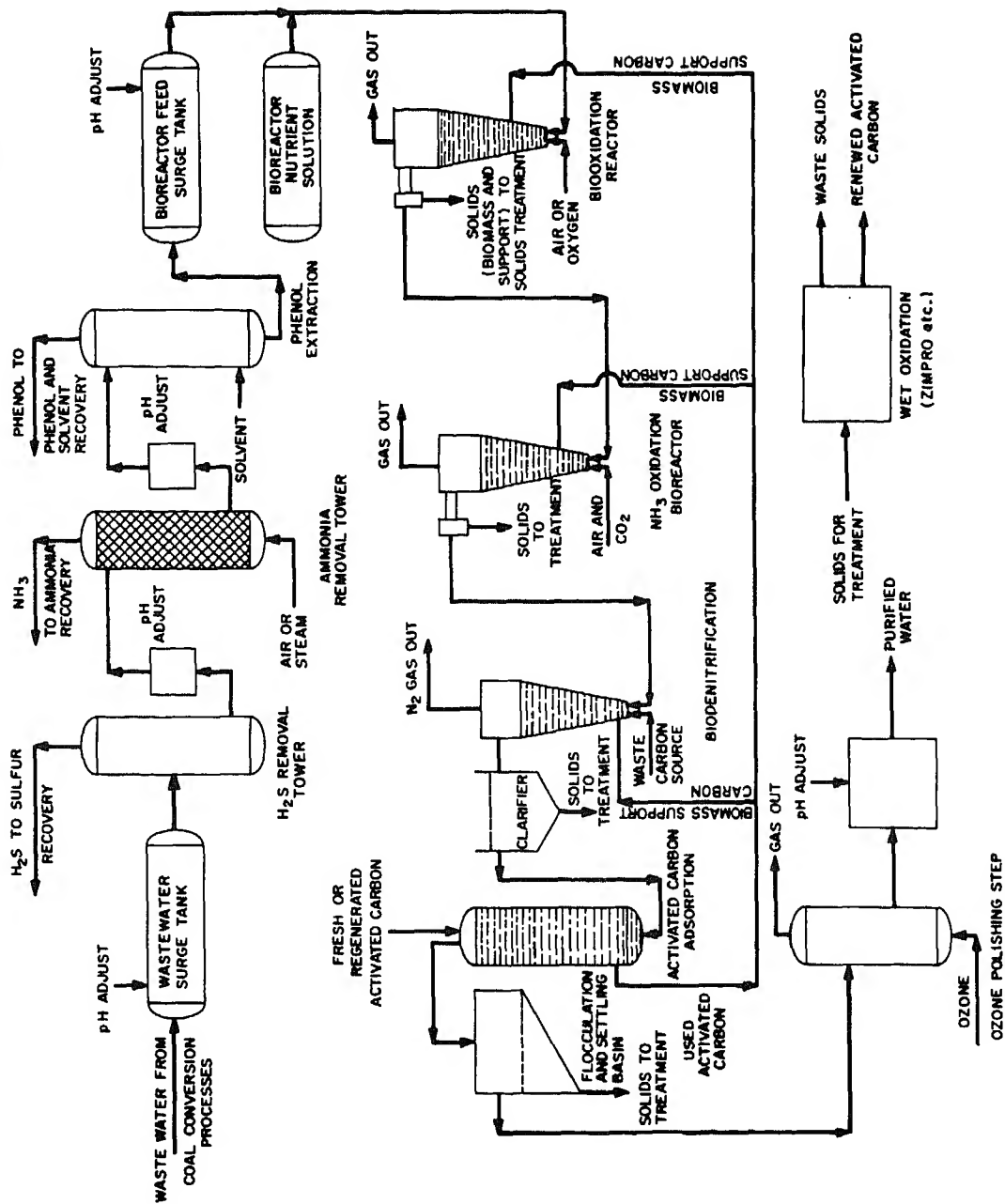


Fig. 2. Proposed integrated flow sheet for treatment of aqueous coal conversion wastes.

balance and economic cost analysis of an integrated control scheme for a commercial-scale, 30,000-ton/day SRC-I coal conversion plant producing ~3000 gal of wastewater per hour.

A tapered fluidized-bed bioreactor that has been adapted to the treatment of coal conversion wastewater is used in the biological step. This tapered fluidized-bed bioreactor system, shown in Fig. 3, consists of a tapered (2.5- to 7.6-cm) section containing a solid support to which bacteria can adhere. The solid support, which is generally a substance such as coal or sand of ~30/60-mesh particle size, is fluidized by the flow of the waste stream to be treated. The tapered bed permits a wide range of fluidizing conditions and allows for expansion of the bed as biomass accumulates on the particles. In addition, the tapered section produces few large eddies and tends to minimize back-mixing when used for two-phase (i.e., liquid-solid) systems.

The chief advantage of the fluidized-bed system is the high concentration of bacteria,<sup>8</sup> which is made possible by the large surface area available on the small particles. Also, particles with excess cells can be easily removed and fresh particles added to the reactor while operation continues. In cases where oxygen is needed for metabolism, the reactor is operated as a three-phase fluidized bed and is sparged with oxygen.

The unit, which has been in operation for more than 1.5 years, has treated the aqueous waste produced by the ORNL Coal Hydrocarbonization Bench-Scale Facility. Some preliminary results indicate that the tapered fluidized-bed bioreactor in a single contacting stage can reduce the phenol and thiocyanate levels in the aqueous waste to  $\leq 1 \mu\text{g}/\text{cm}^3$  and 1 to 5  $\mu\text{g}/\text{cm}^3$ , respectively, at rates up to 5 to 10 kg of phenol and 1.5 to 1 kg of thiocyanate per  $\text{m}^3$  of reactor volume per day at a flow rate of 500  $\text{cm}^3/\text{min}$ . In the fluidized-bed bioreactor using the hydrocarbonization scrubber water as a reactor feed, and when operated for phenol degradation, the total soluble organic content is reduced an average of 95%, whereas phenol is reduced an average of >99.5%. The concentrations of other organic components (PAHs, xlenols, etc.) are also decreased to some extent, depending on the chemical species involved and the residence time available in the reactor.<sup>9</sup>

As a final polishing step to remove any biologically refractive compounds, ORNL is assessing the feasibility of using adsorptive materials other than expensive activated charcoal. Recent investigations have centered on synthetic resins, fly ash, and several lignitic coals. Although the ash and coals do not have the very high adsorptive capacity of activated charcoal, they generally have relatively high surface areas of ~250  $\text{m}^2/\text{g}$ , as measured with  $\text{CO}_2$ .

Both batch sorption tests (isotherm tests) and column screening runs have been performed. In the batch tests, 40 ml of the waste solution and



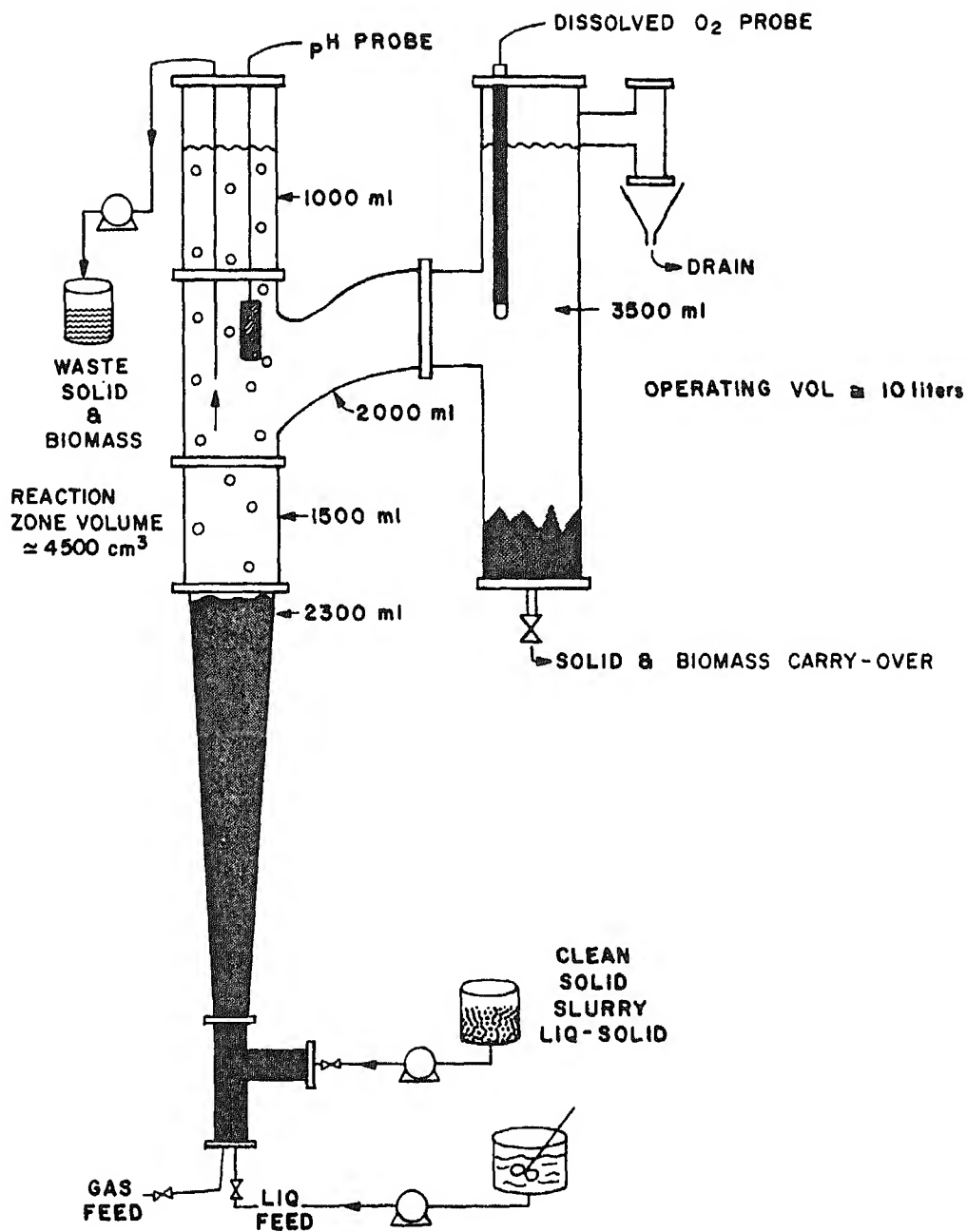


Fig. 3. Schematic drawing of the tapered fluidized bed bioreactor system.

in some of these resins; however, the 4-hr results were not included due to insignificant adsorption.

Column screening tests have recently been performed with two Texas and one North Dakota lignite coals on synthetic wastewater and actual wastewater from the ORNL Coal Hydrocarbonization Facility and a coal tar chemical plant. For the synthetic solutions, both naphthalene and phenanthrene were used as representative, but noncarcinogenic, PAH.

These tests were performed in a packed bed consisting of a 50-ml burette loaded with ~33 g of coal and operated in the upflow mode. The results of one series of tests are shown in Table 3. Because column breakthrough was not reached in most cases, the contaminant loadings reported in Table 3 are minimum values.

Ozonation, an attractive choice for a final cleanup step, is being investigated. In this case, ozonation, normally considered an expensive choice for effluent cleanup, would be used to destroy only those refractory materials that pass through biological treatment. For these screening tests, a small batch ozone reactor was used to treat ORNL biotreated coal hydrocarbonization scrubber water. This system, shown schematically in Fig. 4, consists of a corona discharge ozone generator with a maximum output of 4.5-g/hr, a 1.2-liter reactor, impingers for ozone concentration determination, and a flow-through fluorescence detector. The flow monitor is used to continually follow changes in native fluorescence, which is a gross indicator of the relative abundance of polynuclear aromatic material (PAH). Samples are extracted periodically and analyzed for total organic carbon and phenolic content.

Some preliminary results indicate that ozonation can reduce the phenol and PAH levels in the aqueous wastes to  $\leq 0.1 \mu\text{g}/\text{cm}^3$  and  $\leq 0.25 \mu\text{g}/\text{cm}^3$ , respectively, with contact times of 15 min or less. In the ozone reactor, the phenol and PAH levels were reduced by 95 to 98%. Optimum operating conditions appear to be 20 to 35°C; pH, 11.2; gas flow, ~0.3 liter/min; and inlet ozone concentration, 70-150 mg ozone per liter of oxygen. Outlet ozone concentration and fraction ozone utilized were not measured. The effects of flow rate, pH, and temperature on rate of fluorescence decrease are shown in Figs. 5 to 7.

#### 4. ONGOING WORK

The objective of our present work is to characterize the effectiveness of the various treatment systems for the cleanup of aqueous coal conversion wastes. Since a number of these concepts are still in the developmental stage, an integrated procedure has been formulated to test

Sorbent	Naphthalene (ppm)		Anthracene (ppm)		Benzantracene (ppm)		Phenanthrene (ppm)	
	0.3	3.0	0.0375	0.075	0.002	0.01	0.232	1.16
Activated carbon, 1 mg								
4 hr	0.79	0.78	0.73	0.50	0.88	0.90	0.91	0.43
16 hr	0.88	0.96	0.87	0.90	0.94	0.95	0.90	0.77
Resins, 16 hr								
Chelex 100, 1 g	0.69	0.22	--	--	--	--	--	--
IR-120, 1 g	--	0.58	--	--	--	--	0.78	0.93
IRA-400, 1 g	0.83	0.92	--	--	--	--	1.00	1.00
0.1 g	0.40	0.41	1.00	0.97	1.00	0.90	0.97	0.84
AG-MP-50, 1 g	--	--	0.80	0.75	--	--	1.00	0.92
Ash, 1 g, 4 hr								
John Sevier fly ash	--	0.68	--	--	--	--	--	0.93
Kingston fly ash	--	0.78	--	--	--	--	--	0.96
Wyodak hydro- carbonization ash	--	0.59	--	--	--	--	--	0.89
-----								
Hydrocarbonization wastewater								
Phenol 4.0 (ppm)    Total carbon (107 ppm)								
Texas lignite 1 g, 3 hr			0.20		0.10			

Table 3. Adsorption of contaminants from wastewater in a packed column<sup>a</sup>

Sorbent	Solution tested	Concentration (ppm)	Flow rate (mL/min)	Coal loading (mg/g coal)	Rem (%)
North Dakota lignite	Naphthalene	3.0	6.0	1.6	}
Texas lignite	Naphthalene	3.0	5.0	2.2	
North Dakota lignite	Phenanthrene	1.16	5.0	1.0	
Texas lignite	Phenanthrene	1.16	1.2	0.4	
Texas lignite	Phenol	200	6.0	2.1	}
Texas lignite	Phenol	50	1.2	1.8	
North Dakota lignite	Coal tar Wastewater	55 <sup>b</sup> 1 <sup>c</sup>	1.2	0.8 <sup>b</sup>	
Amberlite XE-348 carbonaceous resin	Phenol	200	6	112	~
ORNL hydrocarbonization char	Phenol	200	6	~0	~
Texas Wilcox lignite	Hydrocarbonization water	107 <sup>d</sup> 4 <sup>e</sup>	1.3	1.5 <sup>d</sup> 0 <sup>e</sup>	~

<sup>a</sup>All tests run in a standard 50-mL burette with ~33 g of sorbent.

<sup>b</sup>Total carbon.

<sup>c</sup>Polynuclear aromatic hydrocarbon.

<sup>d</sup>Total organic carbon.

<sup>e</sup>Phenol.

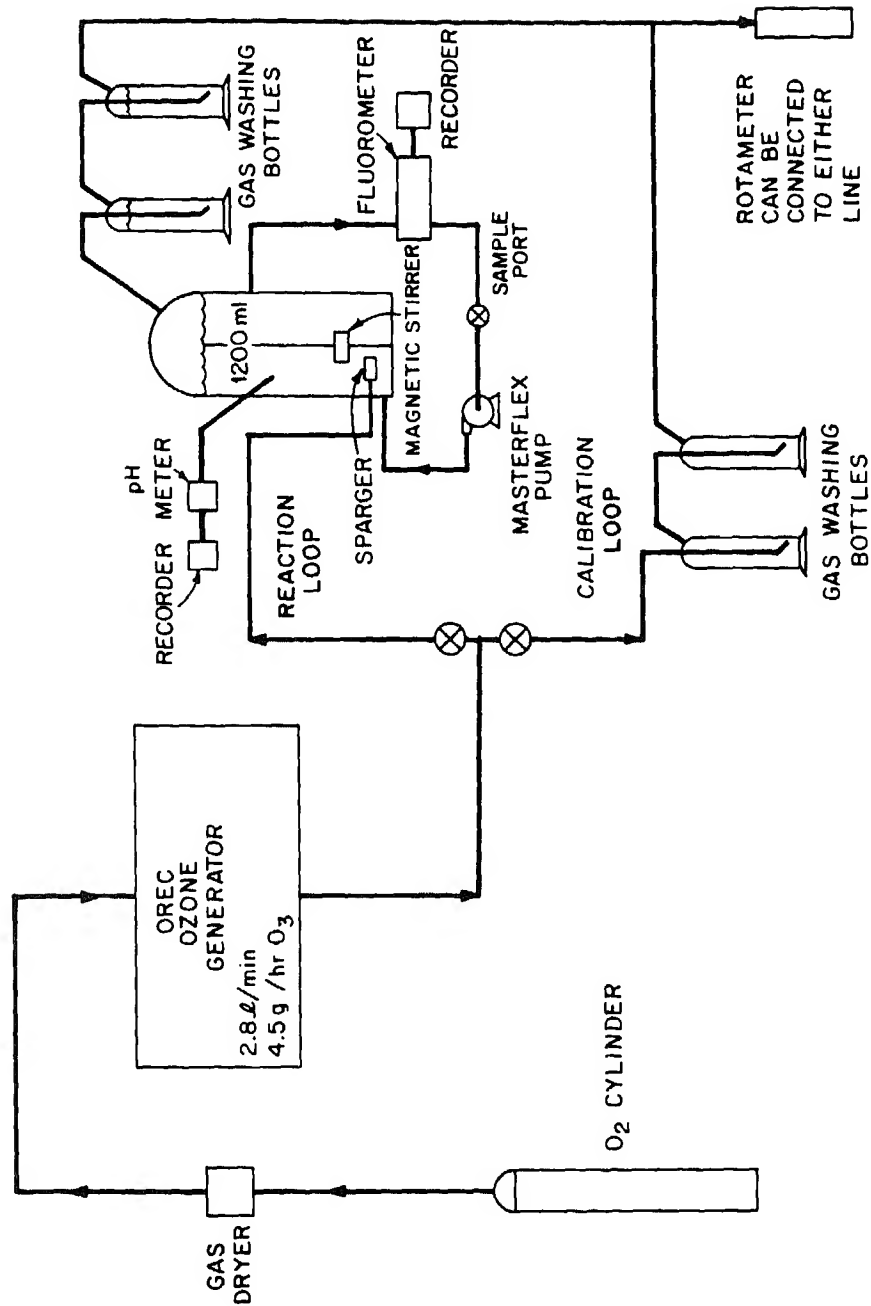


Fig. 4. Schematic drawing of batch ozonation system.

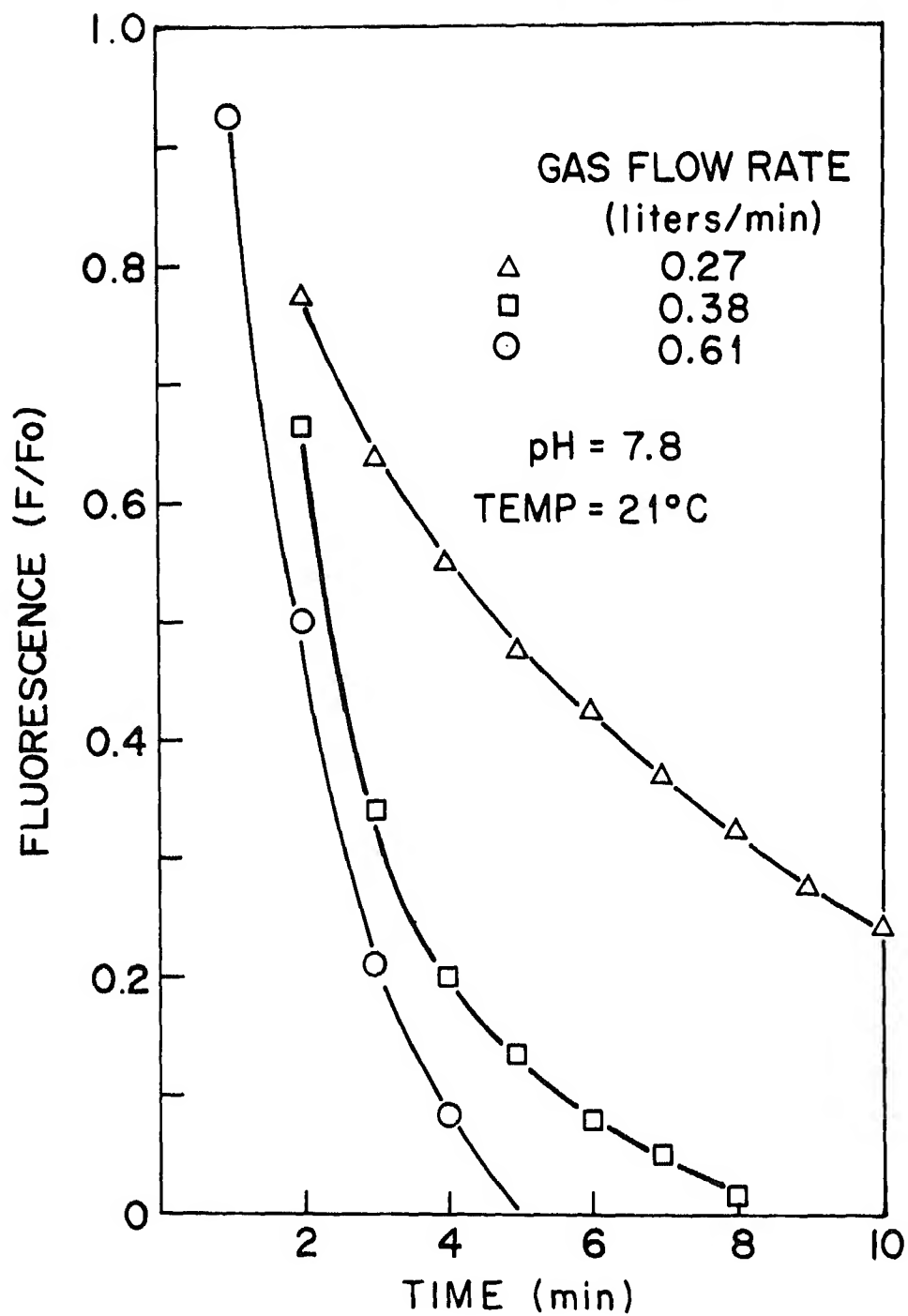


Fig. 5. Ozonation of hydrocarbonization wastewater.  
Effect of gas flow rate.

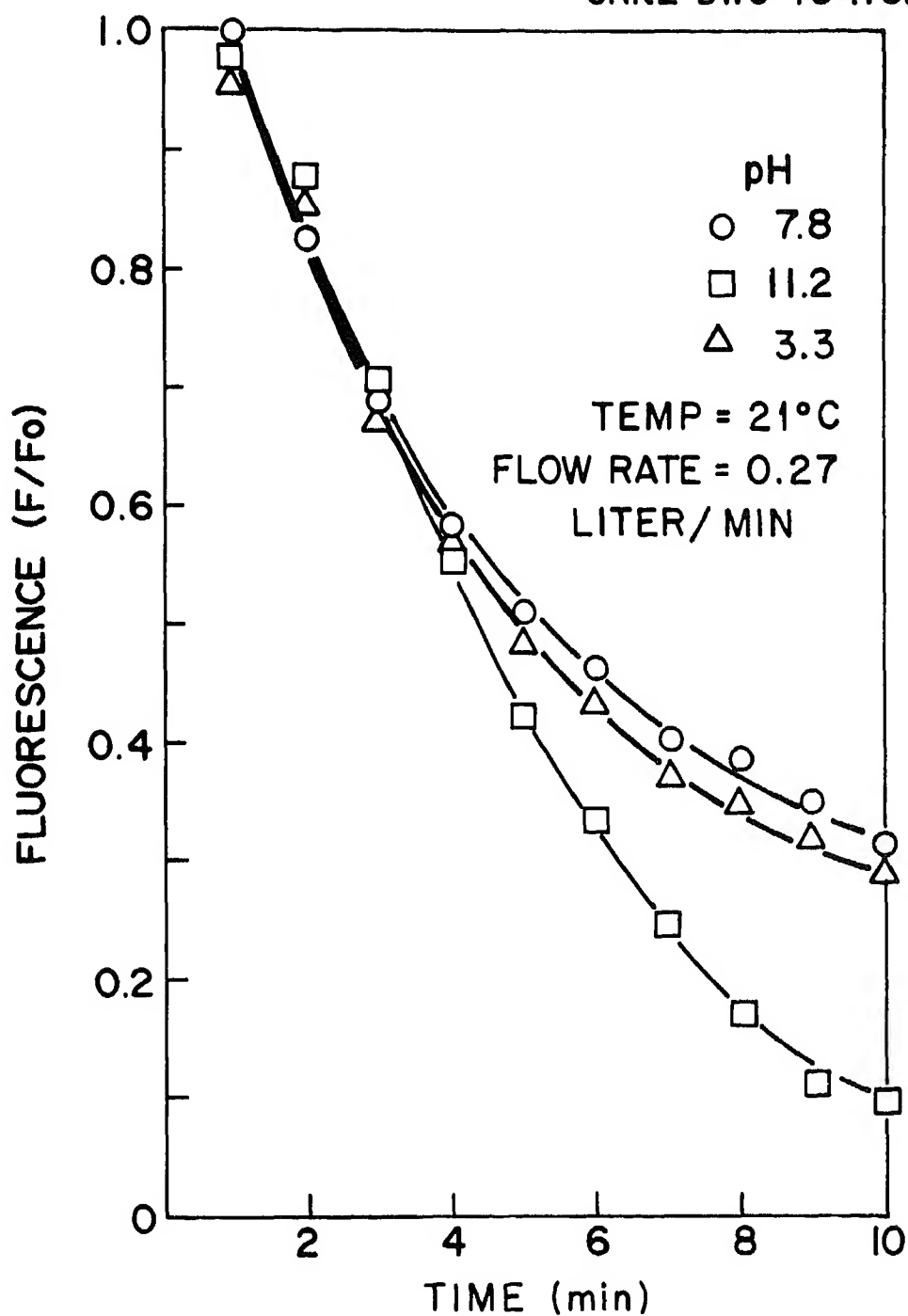


Fig. 6. Ozonation of hydrocarbonization wastewater.  
Effect of pH.

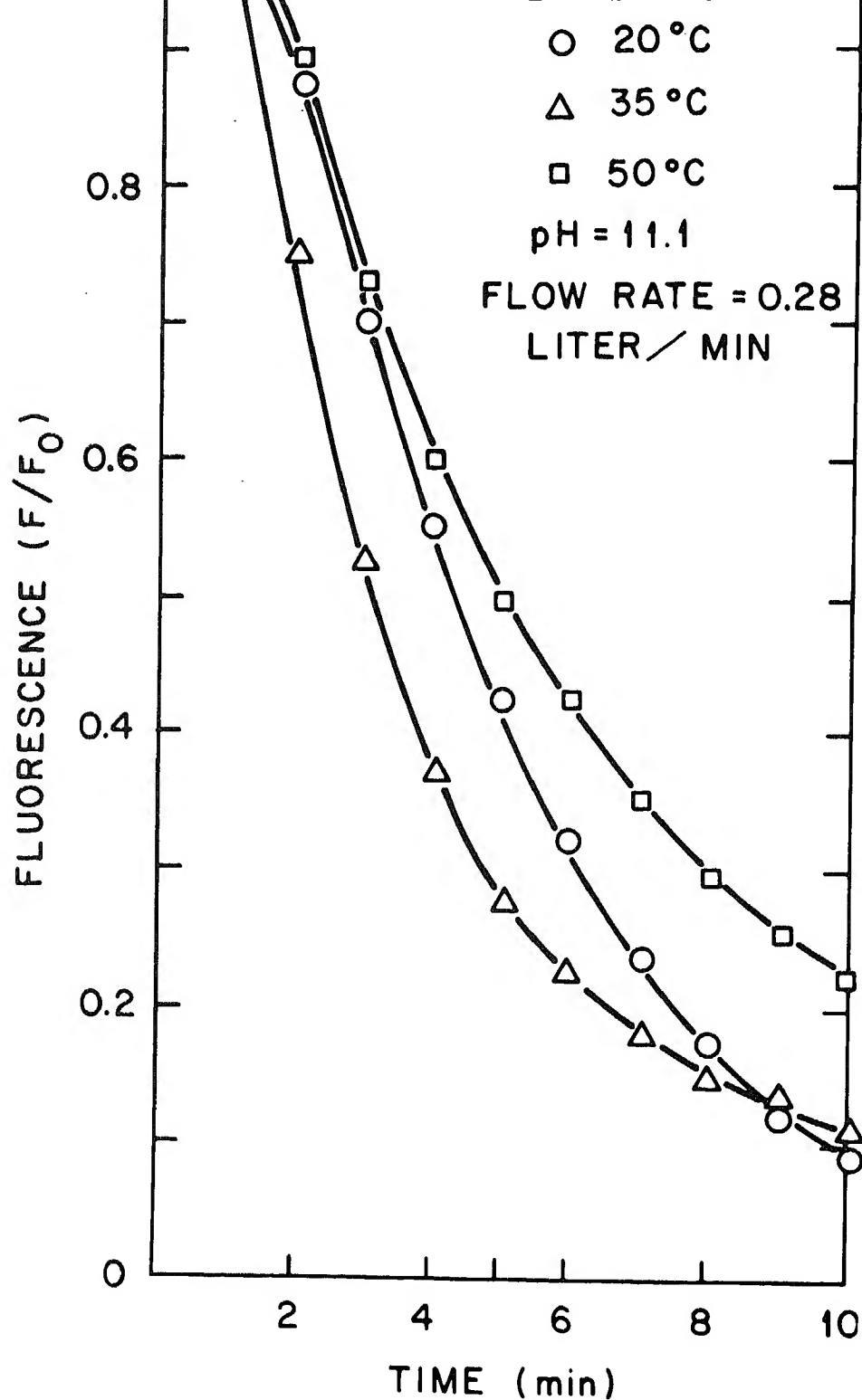


Fig. 7. Ozonation of hydrocarbonization wastewater.  
Effect of temperature.



for characterizing the efficiency of environmental control methods for any coal conversion effluent. For the initial effort, untreated, biotreated, and fully treated material from ORNL's hydrocarbonization experiments will be analyzed, fractionated, and tested for both acute and mutagenic toxicity.

Future studies will continue to concentrate on removing toxic organic and carcinogenic compounds. However, additional work will include integrating the individual cleanup methods into a complete cleanup system similar to the one shown in Fig. 2.

## 5. CONCLUSIONS

Although several gasifiers are being developed that are theoretically capable of being operated under conditions in which they should produce little, if any, aqueous discharge, most of the developing coal conversion processes will produce large quantities of effluents. Because any sour gas cleanup or wet scrubber will transfer pollutants to a water stream, aqueous discharges will be of great concern and will contain sizeable amounts of known toxic and carcinogenic compounds. Present standards do not call for specific levels of treatment; however, future standards will surely be more stringent and will mandate extensive control technology.

The screening of a number of available control technologies has demonstrated that a combination of control technologies can conceivably be used to produce an acceptable effluent water stream. To date, however, these technologies have not been tested on actual wastewater in the field. Several coal conversion processes are presently being considered for demonstration-level projects. If indeed the purpose of these projects is to demonstrate the commercial feasibility of these processes, then it should also be desirable to demonstrate their environmental acceptability.

Wastewater processing trains incorporating some of both presently available and advanced techniques should be constructed and used to treat various coal conversion wastewaters. Although it is not practical to design these pilot treatment processes to treat all the wastewater from any of the various demonstration plants, they should provide data on the treatability of actual wastewater streams and allow evaluations of the various technologies.

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## ABSTRACT

Since 1972 the Laramie Energy Technology Center (LETC) has been seeking an economically viable process for gasifying coal underground (1-7). The LETC has been investigating the potential environmental impacts associated with underground coal gasification (UCG) at four UCG test sites near Hanna, Wyoming (8-10). The Hanna III experiment (5-7) was designed to provide information on the potential impact of UCG on groundwater quality and the environmental control technology implications of those impacts along with parameters critical to the process itself. Environmental objectives were: (1) to characterize the pertinent aquifers, (2) to determine preoperational water quality in the aquifers, and (3) to assess the impacts of UCG on groundwater quality.

## INTRODUCTION

The first United States field test of in situ or underground coal gasification (UCG) were started in 1947 by the U.S. Bureau of Mines (11-14) at Gorgas, Alabama and lasted through 1958. The overall results of these tests were disappointing because seam thickness and coal type were not favorable for UCG. In addition, the economic climate was poor because of the availability of large quantities of cheap oil and natural gas.

Gulf Research and Development Company (15) conducted a small test in western Kentucky in 1968. The test produced a very high heating value product gas for an air injection system, but the reaction was limited to devolatilization. The test also showed that air injection pressures above overburden pressure could be used to enhance the permeability of the coal seam.

The current U.S. program was developed in the early 1970's, but differs from the earlier programs in being highly instrumented, modeled, and analyzed. This program addresses coals of different ranks, geographical areas, angles of dip, operational techniques, and product gas utilization. All processes under development are designed to complement surface technologies and recover the resource that is either too thin, deep, or steeply dipping for the conventional recovery methods.

with the WCT Program divided into the Western Low Btu Gas/Air (WLBG) and Western Medium Btu Gas/Steam-Oxygen (WMBG) Projects.

The WLBG Project (1-10) has been conducted by the Laramie Energy Technology Center (LETC) since 1972 near Hanna, Wyoming. The LETC has developed the Linked Vertical Well (LVW) linkage process to increase the permeability of the coal seam. Sandia Laboratories has provided instrumentation and monitoring to LETC since 1974.

The WMBG Project (16-21) has been conducted by the Lawrence Livermore Laboratory (LLL) at Hoe Creek, Wyoming in the Powder River Basin since 1975. LLL has increased the permeability of the coal seam by explosive fracturing, LVW, and deviated borehole drilling.

The ECT Project (22) which is investigating methods of in situ gasification of near market, swelling coals is directed by the Morgantown Energy Technology Center (METC). The CO-Flow Stream Concept developed by METC is planned for field testing in FY 1980 either at its Princetown, West Virginia test site or at an alternate test site yet to be determined.

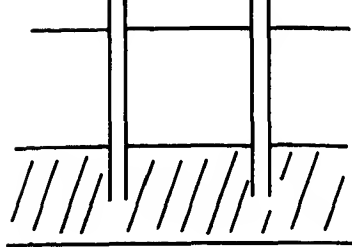
The SDB Technology (coal seams greater than 35 degrees relative to the earth's surface) is being developed by Gulf Research and Development Company near Rawlins, Wyoming, through a DOE contract (23). This first phase of this project (site selection, characterization, and preliminary design) has been completed, and the first field test is planned for late FY 1980.

There are also some active privately funded UCG projects, but they will not be discussed in this paper.

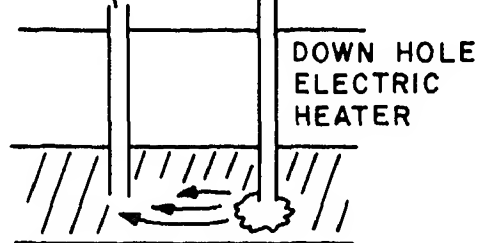
An integral part of the technology development is a program to determine the potential environmental impacts associated with UCG and the control technology that may be needed not only to meet State and Federal environmental regulations but also for end product utilization. This paper will discuss portions of the environmental programs (groundwater and subsidence) associated with the WLBG and WMBG projects.

The LETC has been investigating the potential environmental impacts associated with UCG at its four UCG test sites near Hanna, Wyoming, (Figure 1) on land made available by Rocky Mountain Energy Company (a subsidiary of Union Pacific Railroad). Complementary studies are also being conducted on other types of coal and seams (18-21). Three primary environmental concerns associated with UCG are:

1. Effluent gas quality
2. Surface and subsurface water quality
3. Subsidence effects

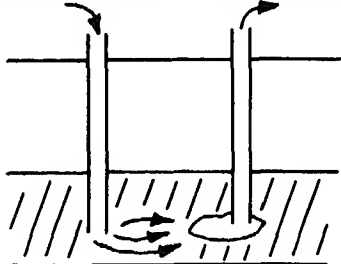


(A) VIRGIN COAL



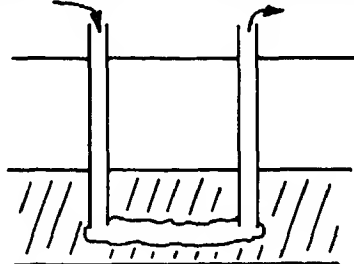
(B) IGNITION OF COAL

HIGH PRESSURE  
AIR INJECTION      GAS  
PRODUCTION



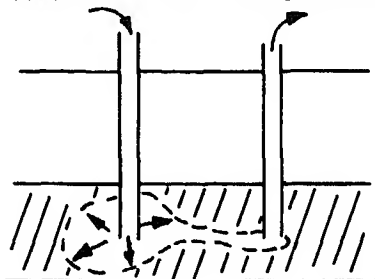
(C) COMBUSTION LINKING FRONT PROCEEDS TO SOURCE OF AIR

LOW PRESSURE  
AIR INJECTION      GAS  
PRODUCTION



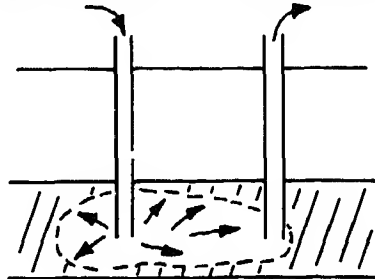
(D) LINKAGE COMPLETE WHEN COMBUSTION ZONE REACHES INJECTION WELL (SYSTEM READY FOR GASIFICATION)

HIGH VOLUME  
AIR INJECTION      GAS  
PRODUCTION



(E) COMBUSTION FRONT PROCEEDS IN THE SAME DIRECTION AS INJECTED AIR

HIGH VOLUME  
AIR INJECTION      GAS  
PRODUCTION



(F) COMBUSTION FRONT EVENTUALLY REACHES PRODUCTION WELL

Figure 1. LVW Process Description

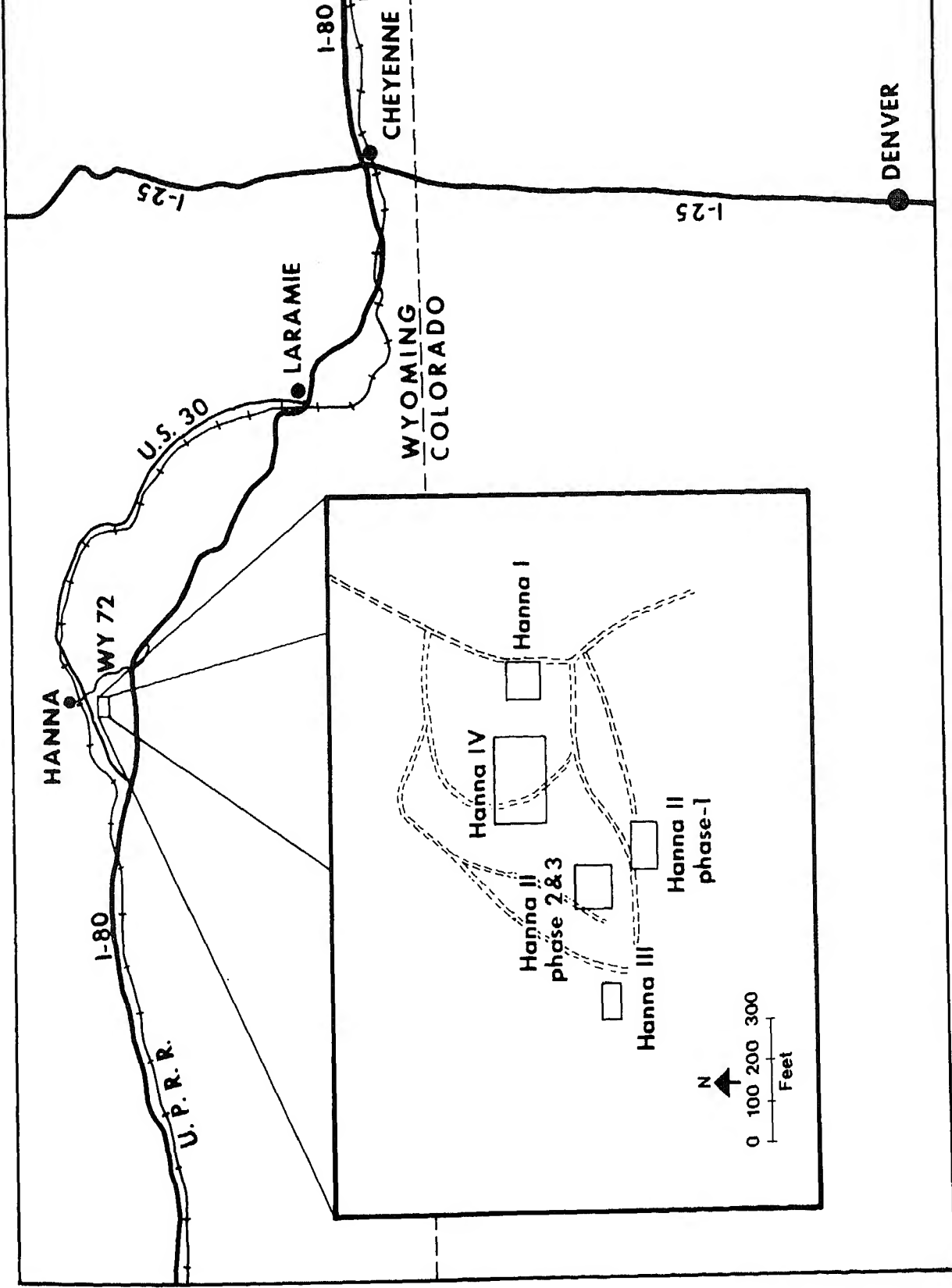
sustain the fire which moves toward the oxygen source, countercurrent to the air flow. As the fire proceeds, carbonization of the coal produces volatiles and leaves a highly porous, permeable pathway between the wells (D). This preparation process, known as reverse combustion linking, is necessary since virgin coal generally does not have sufficient permeability to allow the high air injection rates needed for efficient gasification. Upon completion of linking, high volumes of air are injected at low pressure (E), expanding the combustion zone towards the initial ignition well where the gases generated during linking and gasification are recovered. This expansion generally has a spherical geometry with some distortion toward the production well due to the presence of the linkage pathway. The expansion of the gasification proceeds at a rate of about 1 to 2 feet per day and grows in width up to two-thirds of the well spacing by the time the front reaches the production well. This results in efficient utilization of the coal between the two wells as shown in (F).

The combustible gases produced are hydrogen, methane, carbon monoxide, ethane and propane. Nitrogen and carbon dioxide are also produced, but have no heating value and dilute the product gas. The process yields 120 to 185 Btu/scf gas. This low-Btu gas can be economically produced (24-26) and efficiently used in a gas-fired turbine or a gas-fired steam boiler to produce electric power.

The Hanna III experiment (5-7) was conducted for approximately seven weeks during June and July 1977. About 2800 tons of coal were gasified during the 38 day gasification period with production rates of up to 10 MM scf/day. The average heating value was 138 Btu/scf with an average thermal efficiency of 78 percent for gasification. Water was added to several of the wells during the gasification phase.

### HANNA III OBJECTIVES

The primary objective of the Hanna III experiment was to study the effects of an UCG process on associated aquifers. Three sources of groundwater degradation appear possible. One potential source of degradation results from large amounts of water being removed from the coal as steam with the product gas. This causes the remaining groundwater to carry on increased salt load. Another source of degradation comes from the thermal degradation or transformation of mineral matter within and around the coal seam, with influxing groundwater leaching inorganic salts from these materials thus increasing the inorganic salt load. Organic byproducts produced during carbonization of the coal are swept to the surface with some being left behind as a third source of groundwater degradation. These liquid by-products consist principally of pyridines, phenols, and neutral aliphatic and aromatic hydrocarbons. Any of the organic materials left in the underground system might eventually be dispersed throughout the groundwater regime where communication exists.



**Fig. 2 - LETC's UCG experimental sites**

primarily being conducted to allow determination of necessary environmental control strategy, several parameters critical to the process itself were also examined. Table I lists the specific objectives of the Hanna III experiment.

## EXPERIMENT

The Hanna III experiment can be divided into three phases:

1. Preoperational (Baseline) - Prior to Julian Day (JD) 157,
2. Operational - JD 157 through 211, and
3. Postoperational - after JD 211

with the operational phase divided into three stages:

- a. Start-up - JD 157 through 162,
- b. Linkage - JD 162 through 173, and
- c. Gasification - JD 173 through 211.

Twelve monitor wells were strategically placed within and downdip from the gasification test area (Figure 3). Wells 1 and 2 were the process wells; wells 3, 4, 5 and 14 were monitor wells for the upper aquifer; and wells 6-13 were monitor wells for the coal seam.

Preoperational monitoring of aquifer characteristics and baseline groundwater quality was conducted. Upon completion of this initial characterization work, wells 1 and 2 were linked by reverse combustion, followed by gasification from well 1 to well 2. During the test, temperature, hydrostatic pressures, and electrical conductivities were continuously monitored in each of the monitor wells. (Continuous monitoring of these parameters were planned during the postoperational phase, but the postoperational burn zone conditions have made these probes inoperable and were subsequently removed). The temperatures and pressures yielded data on water level and temperature changes as a function of both time and process parameters.

Three sets of water samples from each of the fourteen wells in the Hanna III pattern plus three sets from Corehole #4 near the Hanna II site (a well cased and completed to the Hanna #1 seam approximately 800 feet NNE of the Hanna III site) were collected, fractionated, and analyzed, prior to the test. Table II shows the components for which analyses were performed and the fractionation and preservation techniques used. Selected samples were analyzed for the organic constituents by GC-MS (Gas Chromatography-Mass Spectroscopy).

The well pattern was also designed to obtain the permeabilities and porosities (transmissivities and storage coefficients) and the continuity and directional nature of both the coal seam aquifer and the overlying aquifer. Data on drawdown and pressure build-up tests were obtained by pumping wells 10 and 1 (in turn) for the seam and well 3 for the overlying aquifer.



## TABLE I

### HANNA III OBJECTIVES

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#### PROCESS

1. TEST PROCESS CONTROL TECHNIQUES
2. DEMONSTRATE PRODUCTION OF CONSTANT HEATING VALUE PRODUCT GAS BY CONTROLLING THE AIR:WATER RATIO IN THE GASIFICATION ZONE
3. IMPROVE THE MATHEMATICAL MODEL

#### ENVIRONMENTAL

1. CHARACTERIZE THE PROPERTIES OF THE COAL SEAM AQUIFER AND OF THE OVERLYING AQUIFER
2. DETERMINE PRE- AND POST-EXPERIMENT WATER QUALITY IN BOTH AQUIFERS
3. ASSESS THE IMPACTS OF UCG ON GROUNDWATER QUALITY

- injection or production well
- well completed into overlying aquifer
- ⊙ well completed into coal seam

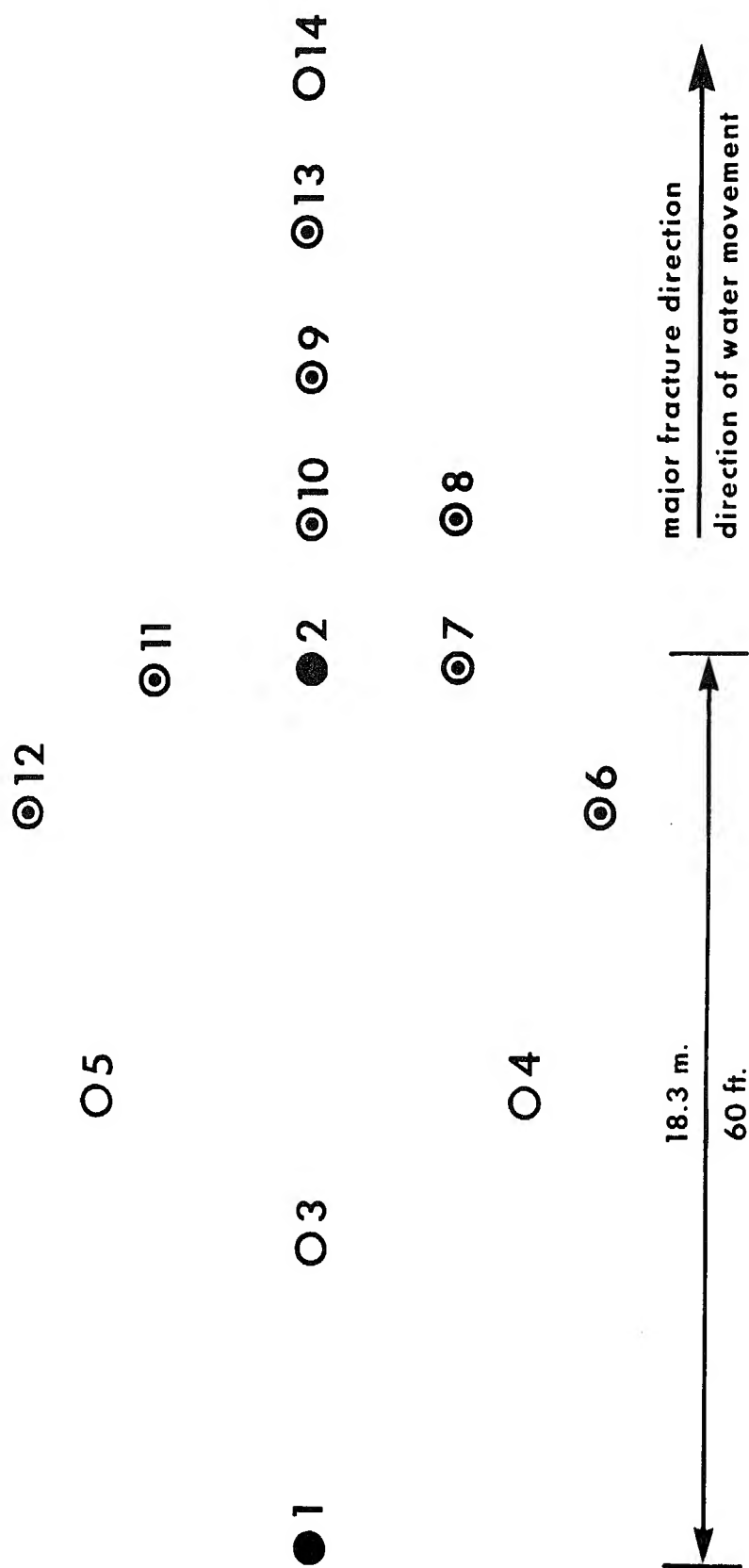


Figure 3. Hanna III

<u>FRACTION</u>	<u>PRESERVATION TECHNIQUE</u>	<u>ANALYSIS</u>
I	COOLED TO 4° C	SO <sub>4</sub> <sup>=</sup> , HCO <sub>3</sub> <sup>=</sup> , CO <sub>3</sub> <sup>=</sup> Si, TDS, TOC, B, TOTAL P, F <sup>-</sup> , Cl <sup>-</sup> , TOTAL INORGANIC CARBON
II	1:8 HNO <sub>3</sub>	Na, K, Ca, Mg, Cd Pb, Zn, Fe, Al, Cu Mn, Mo, Ti, V, As,
III	1:10 H <sub>2</sub> SO <sub>4</sub>	NH <sub>3</sub> -N, TOTAL N, NO <sub>2</sub> <sup>=</sup> -N, NO <sub>3</sub> <sup>=</sup> -N,
IV	CONC. HNO <sub>3</sub> 5% (w/w) K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Hg
V	0.1M Zn(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub>	S <sup>=</sup>

**TABLE II: Hanna III Fractionation and  
Preservation Techniques**

(18-24 months) to determine adsorption rates as a function of time and distance from the source, the extent of the interconnection between the two aquifers, and the groundwater quality changes resulting from migration of leached species.

## RESULTS AND DISCUSSION

### Preoperational

The initial results of the analyses from the 14 wells at the Hanna III site and from Corehole #4 indicated that the waters contain predominantly sodium bicarbonate. The preoperational samples from the wells at the Hanna III site can be differentiated on the basis of total dissolved solids (TDS) levels and well location, i.e., in the coal seam or in the overlying aquifer. A comparison of some water quality parameters of the two groupings is given in Table III. The samples taken from the coal seam show considerably higher TDS levels and higher concentrations of sodium, bicarbonate, and sulfate.

The composition of these waters was such that they produced a high sodium absorption ratio, which would render them unacceptable for irrigation. The residual sodium carbonate levels were also high and indicated alkali problems would develop if this water were used for long-term irrigation. When the quality of the water in the overlying aquifer is compared to the proposed Wyoming Department of Environmental Quality (DEQ) groundwater quality regulations (27), it meets most of the requirements of a Class V water (is or has the potential for being used as livestock water), but the high concentrations of fluoride and mercury may lower this groundwater to a Class VI (is or has the potential for being beneficially used) or Class VII (the potential for beneficial use shall be determined). The quality of the coal seam aquifer meets the DEQ requirements for a Class III water (has the potential for being used as domestic water), but again the fluoride and mercury concentrations may reduce the groundwater to a Class VI or Class VII. Preliminary results of the organic analyses by GC-MS showed that only one sample (Well 13) contained extraneous organic compounds (28).

Pre-operational drawdown tests showed that the two aquifers were not connected. The undisturbed water level in the coal seam was 120 ft. from the surface while the upper aquifer had water 95 ft. from the surface. Thus, the two zones could be tested independently of each other. The calculated axis of major permeability in the Hanna III site lies  $82^{\circ}$  east of north. The average permeability for the seam is about 5 md, but the zone is heterogeneous. The upper zone exhibits an even more marked directional nature or heterogeneity, but its average transmissibility is about the same as that of the coal seam (29).

TABLE III

Comparison of the wells at the Hanna III site (all values reported as mg/l, with the average given first, followed by the range found)

Parameter	Group 1 <sup>a</sup>	Group 2 <sup>b</sup>
TDS (@180°C)	1224 (992-1450)	2614 (1814-3414)
Sodium	496 (238-625)	1107 (759-1455)
Carbonate	33 (0-181)	25 (0-250)
Bicarbonate	1131 (799-1280)	1774 (1274-2274)
Sulfate	35 (1-143)	679 (249-1109)
Total Inorganic Carbon	224 (204-248)	364 (328-400)
Fluoride	1.8 (1.0-3.2)	1.04 (0.54-1.54)
Ammonia (as N)	1.1 (.9-2.1)	1.7 (1.1-2.3)
Boron	0.03 (<0.01-0.11)	0.08 (0.03-0.13)
Total Organic Carbon	41 (31-51)	11 (9-13)

<sup>a</sup> Wells 1, 2, 6, 7, 8, 9, 10, 11, 12, 13 and Corehole 4.

<sup>b</sup> Wells 3, 4, 5 and 14. (Overlying Aquifer)

but responses were observed during gasification. Well 3 responded first, as expected, and within ten days responses were observed in the other wells completed into the overlying aquifer.

The temperature remained constant (45-55°F) during the start up and linkage phase. During gasification temperature increases of about 50°F were observed at wells 6 and 12 from JD 178 to 200, and then at wells 7, 10, and 11 from JD 200 to 204. No temperature changes were observed at wells 8, 9, and 13. This sequence of well response follows the gasification progression from well 1 to 2. (There were no coal seam thermocouples to track the burn progression as in the other Hanna experiments.) Temperature increases in the overlying aquifer (well 3) were observed on JD 198 (Figure 4) which indicated breakthrough into the aquifer. No temperature responses in the other wells were observed.

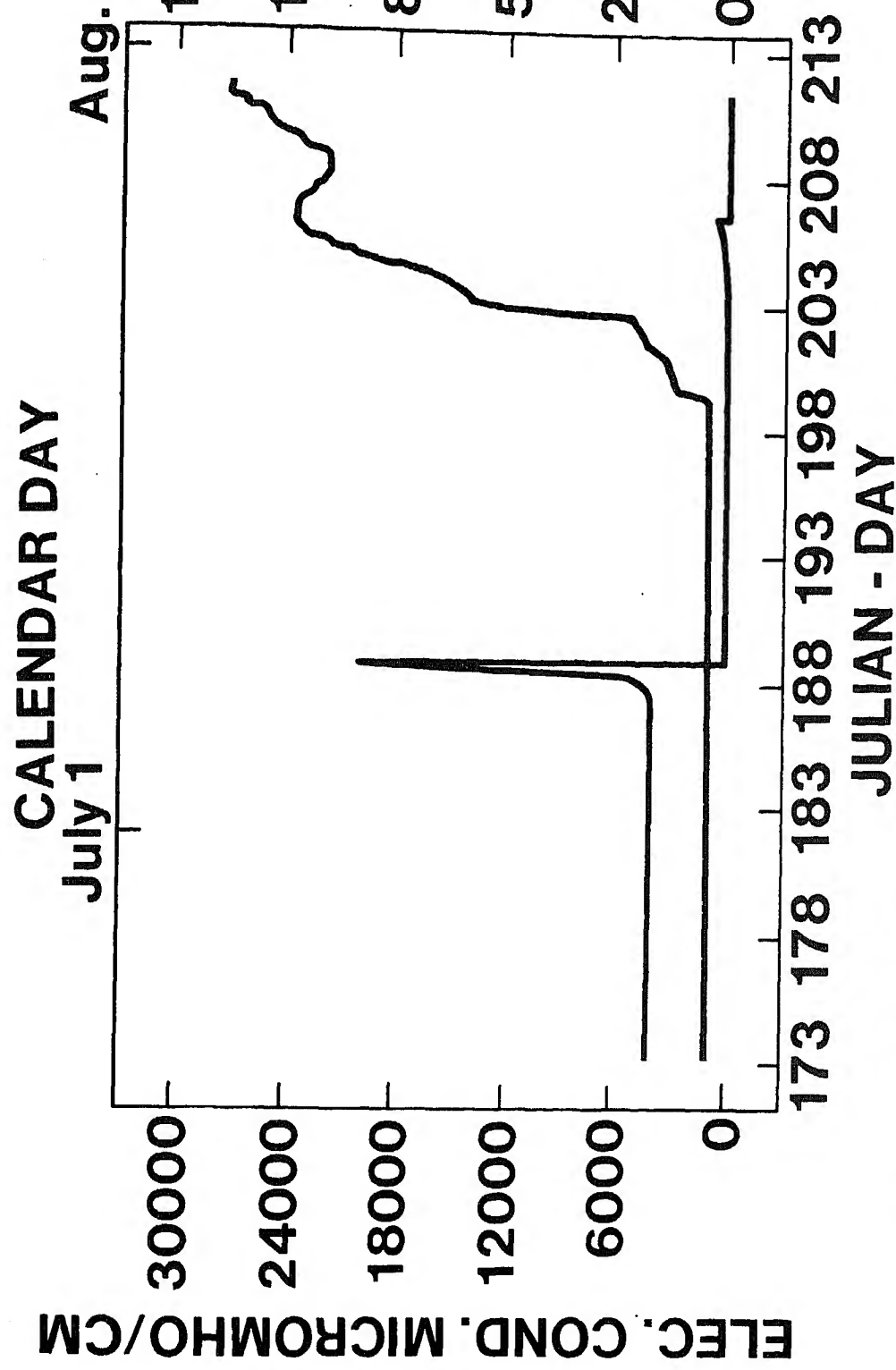
The conductivity probes indicated changes in loading level in wells 9 and 13 during start up. This response probably resulted from the ignition and air injection into nearby well 2, and the production gases following a more permeable zone leading towards wells 9 and 13. During the link, the conductivity of the water in the coal seam aquifer remained constant, and during start up the conductivity of the overlying aquifer remained constant. It is apparent from both the previously discussed linkage temperature data and this conductivity data that the linkage path did not intersect or come close enough to the temperature or conductivity probes to generate a response.

During gasification conductivity responses were observed within the first five days at wells 9 and 13. These wells were also the first to show conductivity responses during start up. Production gases from the gasification zone probably again followed a more permeable zone to these wells. Well 10 located between wells 2 and 9 responded on JD 203. Wells 7, 8, and 11 remained constant.

Increased conductivity levels were observed at well 3 in the overlying aquifer on JD 187 (Figure 4) indicating product gas seepage into the overlying aquifer. Wells 14 and 4 responded approximately five days later, but well 5 remained constant. (Anemolies were observed in the well 5 probes since they were installed).

Hydrostatic pressure, conductivity, and temperature responses at well 3 were observed on JD 184, 187, and 198, respectively. The pressure response indicated that there was communication (fissures and coal shrinkage) between the coal seam and the overlying aquifer. As the gasification cavity increased in size and overburden sluffing continued, additional fractures penetrated into the overlying aquifer allowing product gas into the aquifer resulting in conductivity increases. Finally, on JD 198 additional roofall caused communication between the gasification zone and the overlying aquifer.

Wells 6 and 12 showed opposite temperature and conductivity responses. The temperature increased, remained constant for three weeks (JD 178-200), and returned to its original level. Three days later the conductivity probes



**Fig. 4 - Downhole Conductivity and Temperature Responses for Well #1**

## Postoperational

Early postoperational hydrostatic pressure, temperature, and conductivity data have not been analyzed and interpreted due to computer data retrieval problems. This data will be retrieved and analyzed in the near future.

Preliminary results from the first month's postoperational water quality monitoring appear to indicate that the sulfate and chloride concentrations are decreasing and sodium and total dissolved solids are increasing in all wells. Organic characterization data are not yet available.

## CONCLUSIONS

Preoperational water quality data indicates that the natural groundwater would be unacceptable for short and long term irrigation, and when the quality is compared to the proposed Wyoming Department of Environmental Quality Groundwater Regulations, it may only meet the requirements for a water that has the potential for beneficial use.

Preliminary results indicate that UCG does have an impact on the groundwater. As the monitoring program and data analysis and interpretation progresses, the extent of the environmental impacts will be determined. Once these impacts are known, control and/or utilization technology will be determined.

## ACKNOWLEDGEMENTS

The authors acknowledge Dennis D. Fischer, R. Michael Boyd, A. Eugene Humphrey, S. Bruce King, and David L. Whitman, all formerly of LETC, for their contributions to the UCG program.

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### ABSTRACT

The conversion of coal into combustible gases promises to become an important method of coal utilization. If this conversion is carried out with the coal in place underground - in situ coal gasification - additional environmental and economic advantages can be realized. Our investigations are designed to evaluate some of the environmental implications of this alternative energy technology, and to identify appropriate environmental controls.

Changes in ground-water quality and the possible effects of subsidence and ground movement induced by the underground gasification cavity represent significant environmental concerns associated with the in situ gasification process. We have measured these effects at the sites of two in situ coal gasification experiments conducted in northeastern Wyoming by the Lawrence Livermore Laboratory. Our measurements of ground-water quality in the vicinity of the gasification experiments indicate that the reaction products, such as ash and some coal tars, that remain underground following gasification, are a potential source of localized ground-water contamination. However, the concentration of important contaminants, such as phenols, show a significant decrease due to adsorption by the surrounding coal. Complementary laboratory measurements are providing detailed information concerning this adsorption process.

We have also conducted laboratory and field measurements, in conjunction with modeling studies, to evaluate the effects of subsidence phenomena. Data from subsurface geotechnical instruments installed at the second gasification experiment, as well as measurements of ground-water levels, indicate that roof collapse connected the gasification cavity with overlying aquifers. The environmental implications of this interconnection are being investigated. Our results suggest that hydrogeological site-selection criteria may be of considerable environmental importance in choosing locations for commercial-scale operations.

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the gasification of coal is accomplished with the coal in place underground - in situ gasification - additional environmental and economic advantages can be realized. For example, in situ coal gasification can be carried out without the need for underground mine workers, and it may make recovery of very deep coals economically attractive.

In situ coal gasification generally involves a complex series of chemical reactions, but it can be simply characterized as the heating of coal in the presence of gasifying agents such as oxygen and steam. Some of the coal is burned to provide heat to drive the gasification reactions. In the simplest form of in situ gasification, two or more process wells drilled into the coal seam are used, after the coal is ignited, to inject air or other gasifying agents and to withdraw the resulting combustible gas mixture (Fig. 1). In most cases, the coal's permeability must be enhanced, before gasification, along a path connecting the process wells. (The need to achieve this preliminary connection reliably and economically represents an important current challenge in the development of a practicable in situ technology.) The product gas generally requires some form of clean-up in a surface plant and, if synthetic natural gas is the desired product, an upgrading process to achieve higher energy density.

Although in situ coal gasification offers important environmental advantages when compared with more conventional methods of coal utilization, there are significant environmental concerns that need to be investigated. If these concerns are addressed now, in parallel with the development of the in situ method, it will be possible to identify appropriate control technologies in a timely manner and, perhaps, influence process development such as to preclude or minimize adverse environmental effects.

In order to insure that realistic and effective control methods will be identified, it is essential to develop a quantitative understanding of potential environmental effects as they would occur in connection with large, commercial-sized operations. Some of these possible effects are peculiar to underground gasification and have not been previously investigated in detail. Furthermore, important environmental consequences may require decades to develop. We are therefore concentrating our present efforts on the accumulation of basic data concerning the potential sources of environmental effects, and on the development of reliable, predictive modeling capabilities. With this background, it should be possible to isolate control technologies that are realistically applicable to this promising method of coal recovery.

Two characteristic features of the in situ coal gasification process have led to particular environmental concern: first, the fact that some of the reaction products remain underground as potential ground-water contaminants and, second, the cavity (and possible subsidence) produced by the extraction of the gasified coal. Our in situ coal environmental group at the Lawrence

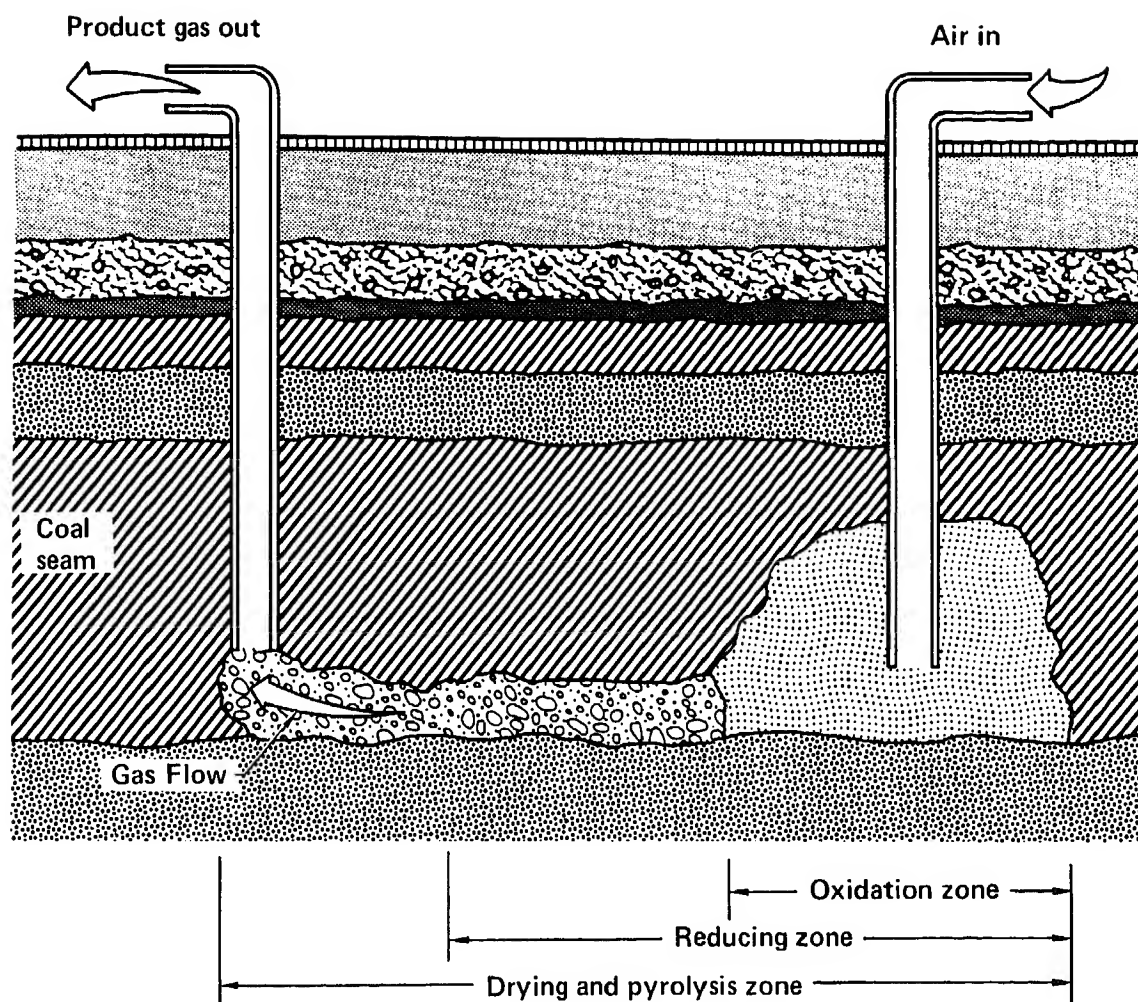


Figure 1. Schematic representation of the *in situ* coal gasification process. The region ahead of the oxidation zone has been modified before gasification to provide a path of increased permeability that will permit adequate gas flow.

consequently, in situ gasification experiments, laboratory investigations, and predictive modeling studies.

LLL has conducted two in situ coal gasification experiments<sup>1,2</sup> at its Hoe Creek site in northeastern Wyoming. These experiments have given us the opportunity to measure changes in ground-water quality and subsidence effects associated with two underground gasification operations.

The Hoe Creek site is located in a sparsely populated region of gently rolling semi-arid rangeland. This area is part of the Powder River basin of northeast Wyoming and southeast Montana - a region that may contain half a trillion tons of coal suitable for in situ gasification. The coal gasified in the Hoe Creek experiments (the Felix II Coal) is 25 ft thick and lies at a depth of about 125 ft - well below the static water level. The Felix II Coal is an aquifer and is overlain by two additional aquifers. A detailed evaluation of the hydraulic characteristics of the Felix Coal and the nearby strata at the Hoe Creek site will be found in reference 3.

The first Hoe Creek experiment<sup>1</sup> took place in the fall of 1976. The two process wells - for injecting air and extracting product gas - were about 33 ft apart, and chemical explosives were used to produce enhanced permeability in the Felix II coal. Approximately 120 tons of coal were gasified in an 11-day experiment.

A second experiment, Hoe Creek II, was conducted during the fall and winter of 1977. The process wells were located approximately 60 ft apart and the required path of enhanced permeability was achieved using a preliminary "reverse combustion" technique, developed in this country by the Laramie Energy Technology Center. The gasification operation lasted 58 days, during which approximately 2000 tons of coal were converted to gas and extracted through the production well. The average energy content of this gas was 108 Btu/scf. Gas losses during this experiment averaged 20%.

Perhaps the most significant environmental concern associated with the underground gasification of coal stems from the existence of gasification reaction products that remain underground. These residual materials include coal ash, char, some of the coal tars, and approximately 10-15% of the product gases which are not extracted through the production wells. When ground water returns to the gasification zone, the ash is leached, producing inorganic contaminants, and some of the other residual materials, including organics are dissolved. The contaminated water moves through the coal seam in the general direction of the natural ground-water flow. Fortunately, there are other natural phenomena - for example, the filtering and adsorption properties of coal itself - which tend to purify the ground water and to restrict the contaminants to a localized region. Nevertheless, the ultimate environmental significance of the residual underground products is not yet known.

The ground movement and potential subsidence associated with the creation of a gasification cavity are also of significant environmental concern - in part, because these phenomena may affect the dispersal of the reaction-product contaminants. In particular, fissuring and roof collapse, which result from cavity formation, can destroy the integrity of the underground "reaction vessel" and permit the escape of pollutants to the surface or into overlying aquifers. Large areal gasification operations could also lead to significant surface subsidence, with results that may be important environmentally, and in their effects on process facilities.

#### WATER SAMPLING AT HOE CREEK I

Measurements of changes in ground-water quality near in situ coal gasification experiments are of importance, initially, in that they help to define the contaminant source. That is, they permit a description of the composition, concentration, and early-time distribution of the underground contaminants. Such measurements also provide information concerning short-term changes in concentration and composition that are a result of chemical reactions, sorption by coal and other media, or biological action. Over a period of several years, the water quality measurements will begin to yield information concerning the possible development of a plume of contaminated ground water that may spread outward from the gasification site in the direction of natural ground-water flow.

We have carried out extensive ground-water quality investigations at the sites of both LLL in situ coal gasification experiments. Approximately a dozen wells in the vicinity of the first gasification experiment (Hoe Creek I) were monitored before, during, and after gasification<sup>4,5</sup>. The samples were analyzed in the field and, much more extensively, at the laboratories of the U. S. Geological Survey, the Research Triangle Institute, and LLL. A simplified summary of the data is given in Table I.

Species	Pre-gasification value (mg/l)	Inside burn zone		Outside burn zone	
		Concentration Increase (mg/l)		Concentration Increase (mg/l)	
Phenols	0.001	0.1	100 x	500	$5 \times 10^5$ x
CN <sup>-</sup>	0.01	0.4	40 x	300	$3 \times 10^4$ x
NH <sub>4</sub> <sup>+</sup>	0.5	20	40 x	70	100 x
DOC	6	4	-	200	40 x
Br <sup>-</sup>	0.1	1.0	10 x	4	40 x
Pb <sup>+2</sup>	0.001	0.001	-	0.04	40 x
Ba <sup>+2</sup>	0.1	-	-	1.0	10 x
K <sup>+</sup>	5	60	10 x	45	8 x
Li <sup>+1</sup>	0.03	0.3	10 x	0.2	6 x
Mg <sup>+2</sup>	10	50	5 x	60	6 x
SO <sub>4</sub> <sup>-2</sup>	200	2000	10 x	1000	5 x
Ca <sup>+2</sup>	40	600	20 x	200	5 x
B (III)	0.1	0.7	7 x	0.5	5 x

Among the chemical species that show a large increase as a result of the gasification experiment are the phenolic materials, which represent the largest group of organic contaminants introduced into the underground environment by this experiment. The changes in concentration of the phenolic materials, as a function of time and distance from the boundary of the gasified zone, are shown in Fig. 2. Notice that the phenol concentrations have decreased by roughly two orders of magnitude at all distances from the burn zone. Although most other contaminants are also decreasing<sup>5</sup>, their rates of decrease are not, in general, as rapid as those indicated in Fig. 2.

The water from selected wells was analyzed by the Research Triangle Institute using a method that combines gas chromatography and mass spectrometry (GC-mass spec). This technique (now also employed at LLL) provides detailed information concerning volatile and semi-volatile organic contaminants. The coal gasification process produces an enormous variety of such organic by-products. The more volatile aromatic materials such as benzene, toluene, xylenes, and naphthalene penetrate into the porous media surrounding the gasification zone.<sup>5</sup> As illustrated in Fig. 3, the species of lower molecular weight (more volatile) are transported further from the gasification zone. A discussion of some limitations that apply to quantitative comparisons of the GC-mass spec data with results obtained by other methods will be found in Ref. 5.



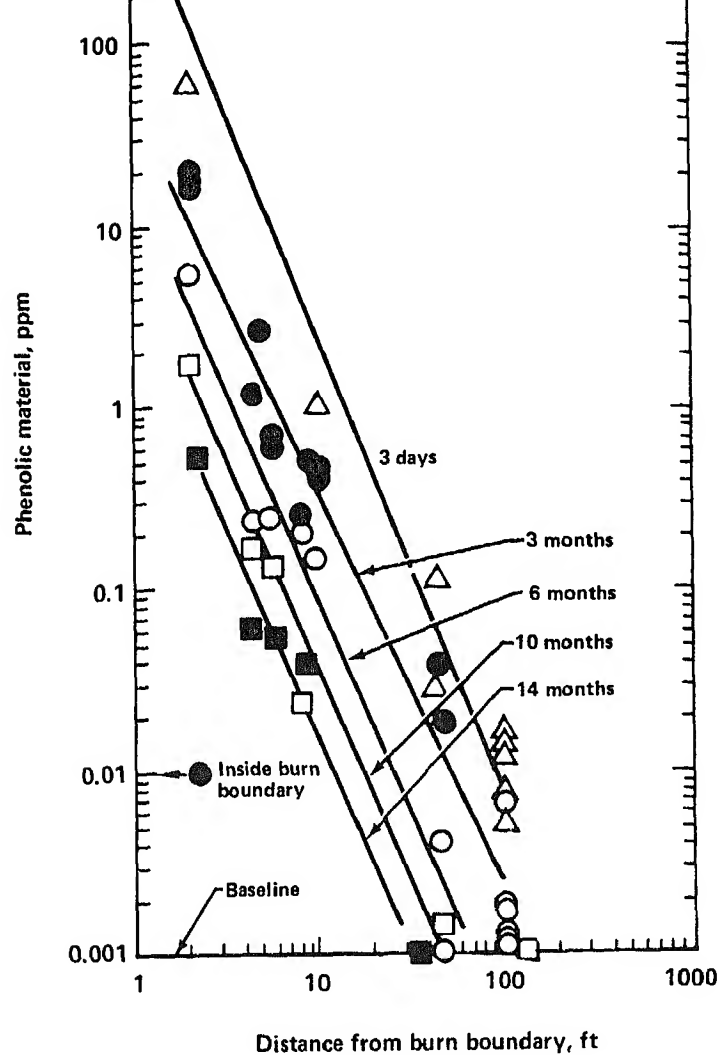


Figure 2. Concentrations of phenolic materials as a function of distance from the nearest burn boundary of the Hoe Creek I *in situ* coal gasification experiment. Times are measured from the end of gasification. Sampling wells are completed in the gasified coal seam and located in various directions from the gasification zone.

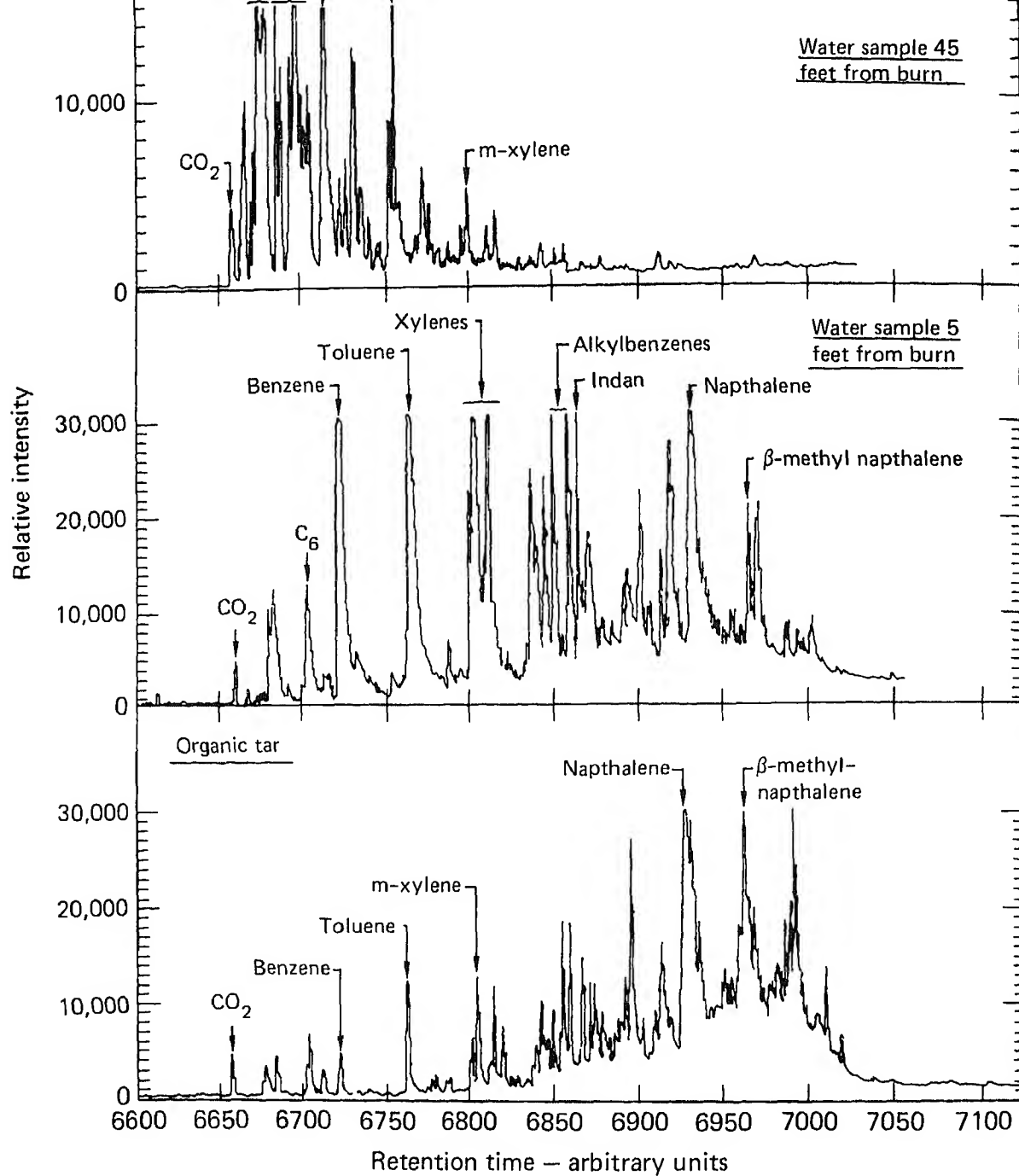


Figure 3. Chromatograms of volatile organics found in product tar and in water obtained 5 ft and 45 ft from the burn zone. The numbers on the abscissa are related to the chromatograph retention times. Note that the lower-molecular-weight (more volatile) species move much further out into the formation, and that the organics in the nearby water are more like the product stream tar.

provide evidence concerning changes in contaminant concentrations that may occur as a result of natural ground-water flow. In principal, phenol concentrations in the outer wells might ultimately increase. Nevertheless, the rapid and uniform decrease in the concentrations of phenolic materials over a period of more than a year is an encouraging example of the self-cleansing capabilities of coal aquifers.

## LABORATORY AND COMPUTATIONAL STUDIES

A clearer and more quantitative understanding of the ground-water changes near an underground gasification operation can be achieved by means of laboratory investigations carried out in conjunction with the field measurements. Of particular interest, are the nature and magnitude of the cleansing actions that occur when contaminated water is exposed to coal. Results such as those shown in Fig. 4 leave little doubt that phenol is rapidly adsorbed by coal. More elaborate experiments involving the flow of contaminants through a column of coal (Fig. 5) are also underway. They establish values of the distribution coefficient,  $K_d$ , which is a measure of the fractional adsorption of a dissolved contaminant and an essential ingredient in contaminant transport modeling. Our modeling efforts include the development of a 2-dimensional computer code capable of predicting transient dispersion of contaminants introduced continuously from a line source. The model includes convection, longitudinal and lateral dispersion, and adsorption.<sup>6</sup>

## GROUND-WATER EFFECTS AT HOE CREEK II

Nine ground-water sampling wells were provided for measuring ground-water quality changes resulting from the second Hoe Creek experiment. Since the second experiment involved the gasification of 20 times as much coal as Hoe Creek I, it would be of considerable interest to compare ground-water changes near the two sites. Such a comparison might help to establish the dependence of the contaminant source strength on the amount of coal gasified. In particular, the comparison might indicate whether the concentrated "shell" of phenolic materials just outside the burn zone is a surface effect or dependent on the entire gasified volume. Unfortunately, a straightforward and meaningful comparison of ground-water measurements at the two sites is impossible, for reasons discussed below.

We have sampled the ground-water near the Hoe Creek II site before, during, and several times after gasification. Some analyses are performed in the field, and preserved samples are sent for extensive analysis to U.S. Geological Survey laboratories, Gulf South Research Institute, and LLL. The

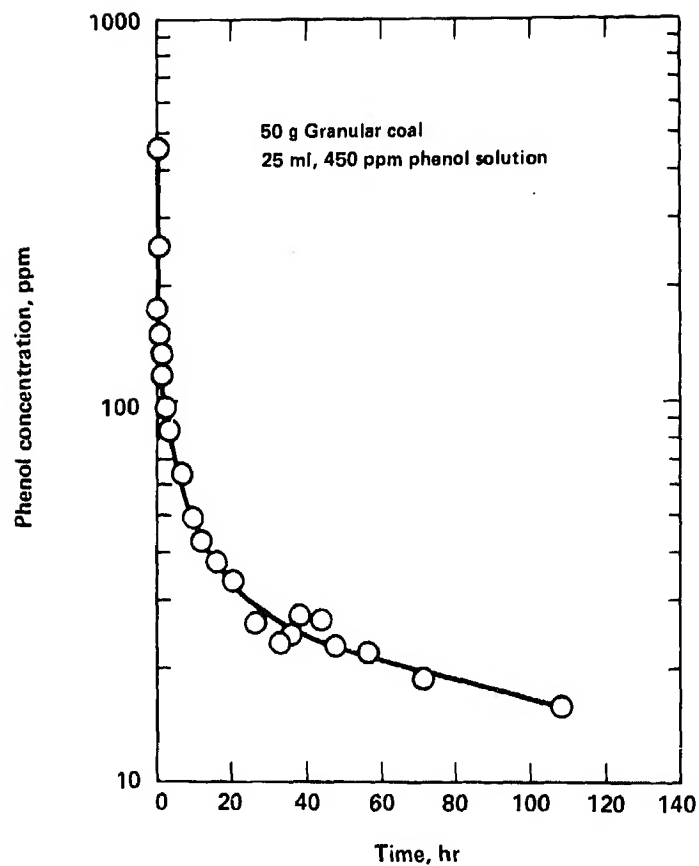


Figure 4. Laboratory measurements of phenol adsorbed by granular coal as a function of time. The data represent the analysis of a large number of equivalent phenol solutions agitated with a shaker table.

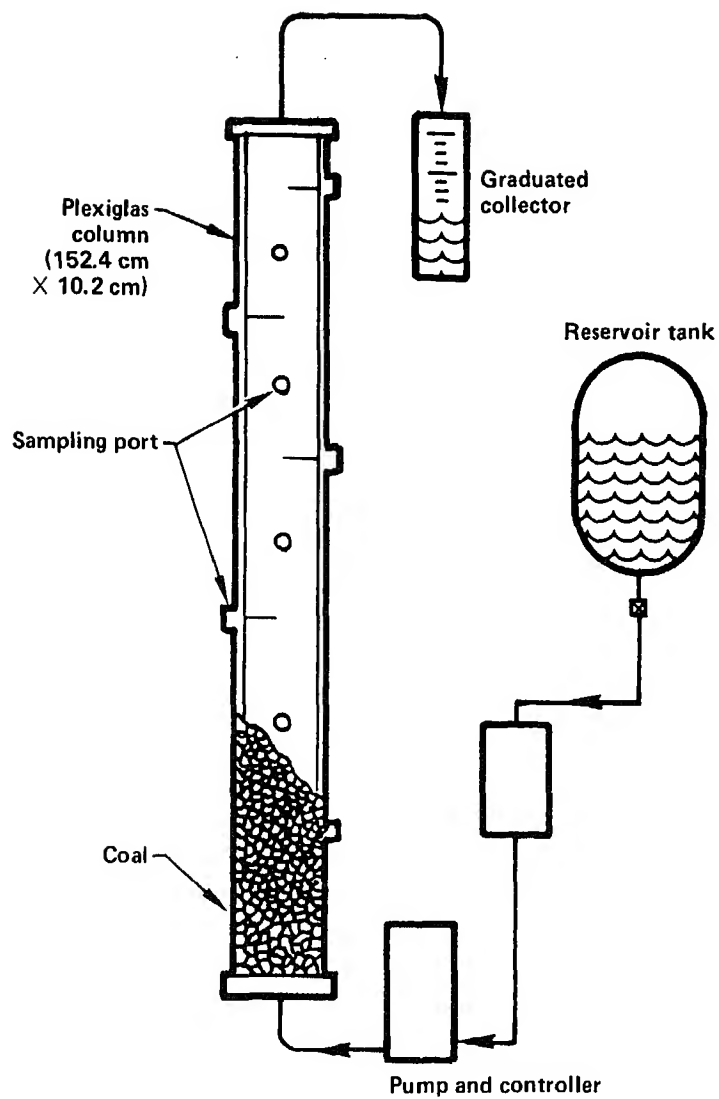


Figure 5. Coal column apparatus used to simulate the flow of contaminated ground water through a coal seam. During operation, samples are extracted through rubber septa using a hypodermic syringe.

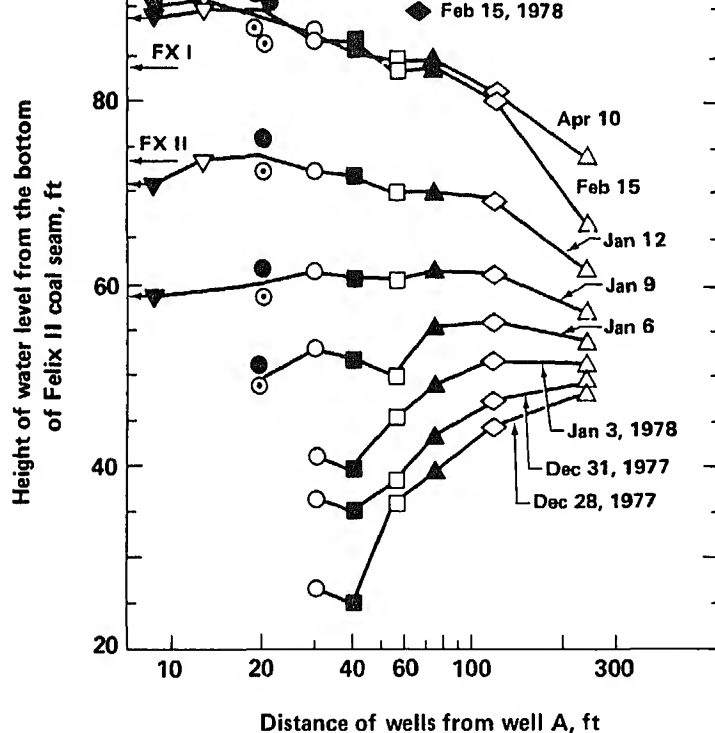
concentrations are expected to depend very strongly on well locations relative to the burn boundary (Fig. 2), and this effect could account for large differences in measured concentrations. However, a more important difference stands in the way of a simple comparison of contaminant levels near the two sites. Water level data (Fig. 6), subsurface geotechnical measurements, and post-burn coring investigations show that cavity roof collapse connected the gasification cavity with overlying aquifers (The Felix I Coal and a coarse channel sand above it). Since the Hoe Creek site is a recharge area (hydraulic head decreasing with depth), water from the overlying aquifers is flowing into the gasification cavity and producing an abnormally high hydraulic head within the cavity. Calculations based on the data of Fig. 6 suggest that ground-water flow rates in the immediate vicinity of the cavity exceed normal flow rates by at least an order of magnitude. Preliminary data on phenol concentrations (Fig. 7) showed a temporary increase in concentration in some of the sampling wells, which are completed in the Felix II Coal. Evidently, source concentrations and source geometry were significantly affected by the aquifer interconnection. The environmental implications of the altered contaminant distribution are being investigated.

Another question whose importance is emphasized by the aquifer interconnection at the Hoe Creek II site concerns the possibility that contaminants from the gasification zone may migrate into overlying aquifers. Additional sampling wells recently completed in the Felix I aquifer will help to answer this question. It may be that the downward flow of water in a recharge area will minimize the spread of contaminants into overlying aquifers. In any case, the importance of an enlightened choice of site selection criteria is becoming increasingly apparent.

## SUBSIDENCE STUDIES

Since ground deformations induced by the gasification cavity may play an important role in determining contaminant dispersal and may, in addition, lead to significant surface subsidence, an improved understanding of these subsidence phenomena is of outstanding importance. We are attempting to extend our knowledge of these effects and develop a reliable predictive capability through a combination of laboratory tests of overburden cores, geotechnical measurements at the site of ongoing gasification experiments, and finite element modeling.

A preliminary modeling study of the subsidence induced by underground coal gasification was conducted in preparation for the first Hoe Creek experiment. In the treatment employed, a stratified overburden is stressed by gravity loading and by the removal of coal seam elements in a manner simulating coal combustion. The resulting stresses, strains, and displacements are determined for the duration of the excavation process and for subsequent quiescent periods during which plastic deformation and stress relaxation gradually take place in the rock and soil strata. Inelastic



$\triangle$  = WS9,  $\diamond$  = WS8,  $\blacktriangle$  = WS7,  $\blacklozenge$  = Well B,  $\square$  = WS6,  $\blacksquare$  = WS5  
 $\circ$  = WS4,  $\odot$  = WS3,  $\bullet$  = WS2,  $\nabla$  = WS1 (in Felix I),  $\blacktriangledown$  = Well A  
 FX I = water level of the aquifer in Felix I  
 FXII = water level of the aquifer in Felix II

Figure 6. Water levels in wells near the Hoe Creek II *in situ* coal gasification experiment. The water levels are plotted as a function of distance from the injection well "A" at various times following gasification. (A logarithmic distance scale is used to avoid data crowding for the close-in wells.) All wells are completed in the gasified Felix II coal seam except WS-1, which was completed in the overlying Felix I coal aquifer. The data show how water levels have changed since air injection was terminated at the conclusion of the gasification experiment on December 25, 1977. The elevated water levels in the vicinity of the gasification zone suggest that the gasification cavity has been interconnected with the overlying Felix I coal aquifer, which lies about 20 feet above the Felix II Coal, and with another aquifer above the Felix I Coal.

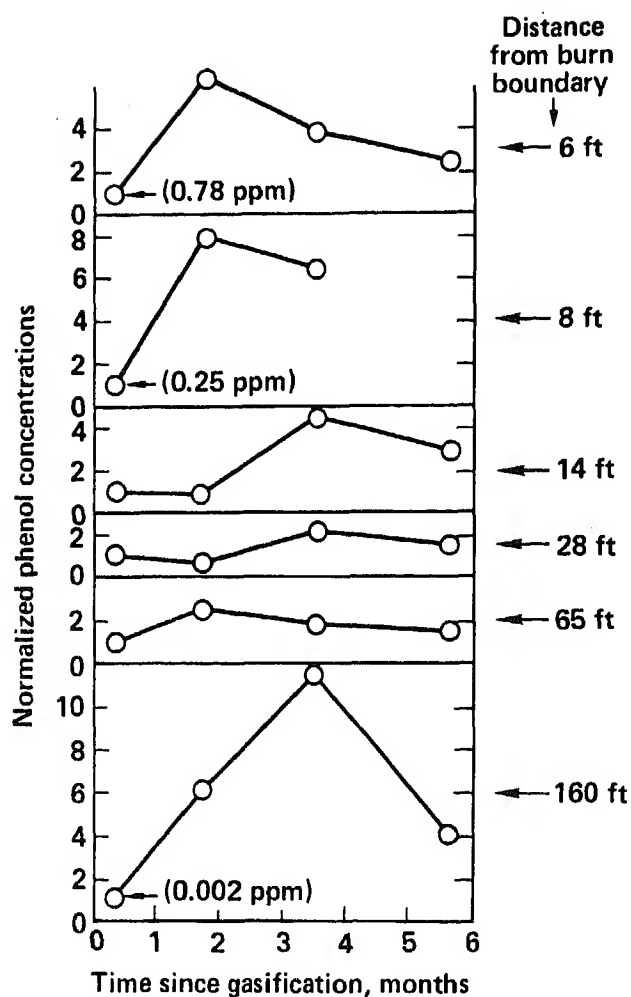


Figure 7. Changes in the measured concentrations of phenolic materials in the Felix II coal aquifer as a function of time after gasification. The measurements were made in some of the wells shown in Figure 5. These and other data suggest that the contaminants are moving outward away from the gasification zone. This movement appears to be much exaggerated in the immediate vicinity of the gasification zone as a result of an interconnection with an overlying aquifer. (Note that the actual magnitudes of the phenol concentrations measured in the close-in wells are hundreds of times greater than those in the outermost well.)



subsidence was detected.

An augmented version of the above method was used in an effort to predict subsidence and ground movement for the Hoe Creek II experiment.<sup>8</sup> Two sets of assumed values of material properties were employed, termed "probable" and "lower bound". We also added a new feature to our method of modeling the excavation process associated with gasification. As the computations proceeded, roof material that developed tensile stress was mathematically removed in a subsequent iteration. In other words: as coal elements were "gasified" and zones of tensile stress appeared in the roof, those zones were "spalled" or allowed to collapse. This procedure produces a shallow arched roof, free of tensile stress, such as might be expected to occur naturally.

This augmented model also predicted surface subsidence of only an inch or so. On the other hand, relatively large deformations, and considerable roof caving were predicted below the surface. It seemed clear that subsurface measurements would produce the most helpful data - both for understanding the implications of subsidence for the in situ gasification process, and as a guide in checking and improving our subsidence modeling capabilities. Subsequent measurements have shown that a combination of roof caving and combustion (in the overlying Felix I Coal) caused portions of the cavity to be extended some 70 ft above the top of the Felix II Coal, much higher than predicted.

In an effort to provide subsurface data, we designed an array of geotechnical instruments for installation in the overburden at the site of the Hoe Creek II experiment (Fig. 8). The instruments included two 6-position borehole extensometers (Fig. 9), two electrical shear strips, a multiple piezometer installation, and a borehole deflectometer apparatus that was utilized in six specially cased boreholes. Provisions for surface measurements included specially designed isolation bench marks, an optical level, and a precision tape extensometer. A detailed description of these instruments, their deployment at the Hoe Creek II site, and some preliminary results are reported by Ganow et al. in reference 9. An analysis of the geotechnical data (obtained before, during, and after the Hoe Creek II experiment) has provided a relatively clear picture of the overburden deformation and roof collapse that occurred in response to the growth of the gasification cavity. Of particular interest, is the fact that the extensometers and piezometers documented the interconnection of the gasified coal seam with the overlying Felix I and channel sand aquifers.

Since a variety of measurements have shown that roof collapse extended significantly higher than predicted, we are attempting to develop modeling methods that take account of process-related phenomena that may be significant. Roof spalling due to shrinkage effects induced by heating may be an important factor in determining the ultimate cavity size. A preliminary attempt to incorporate these shrinkage effects into the calculations is described by Greenlaw et al. in reference 10.

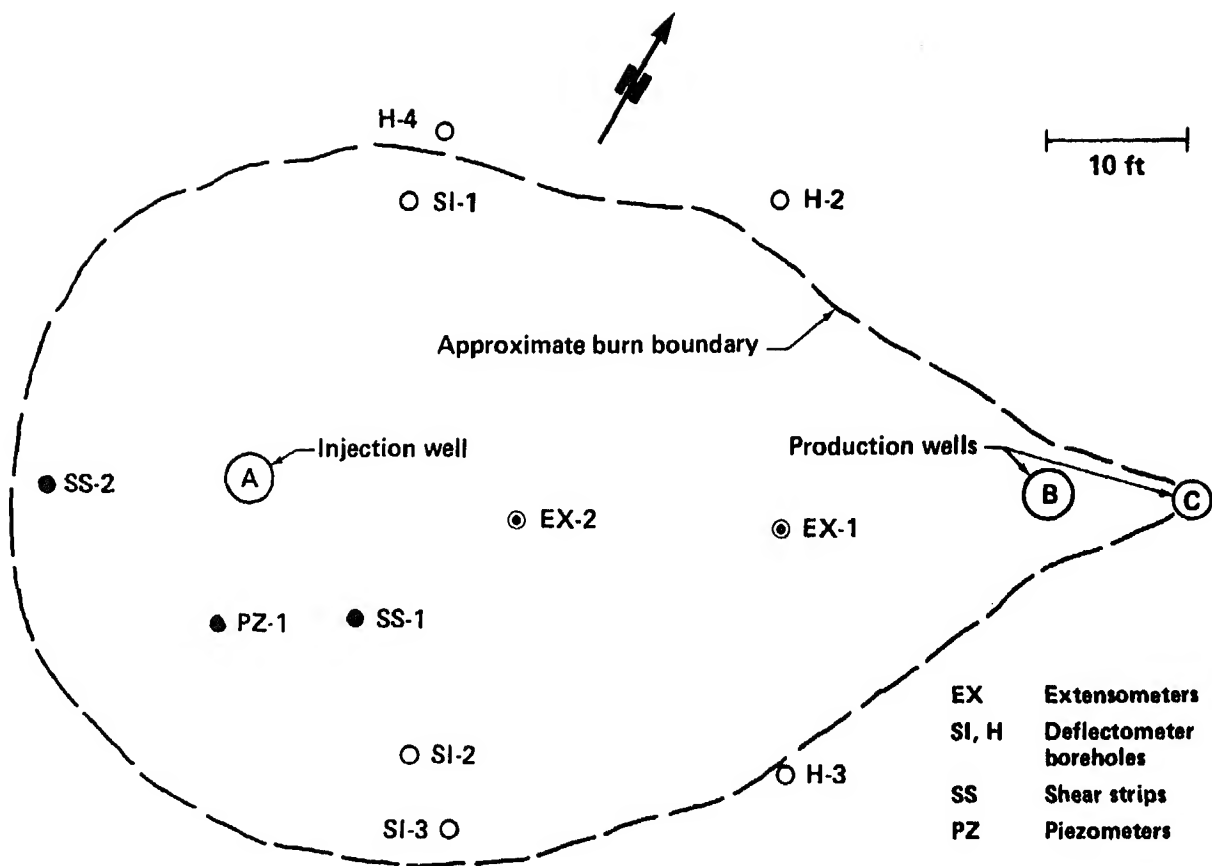


Figure 8. Plan view showing process wells and subsidence instrumentation boreholes at Site II.

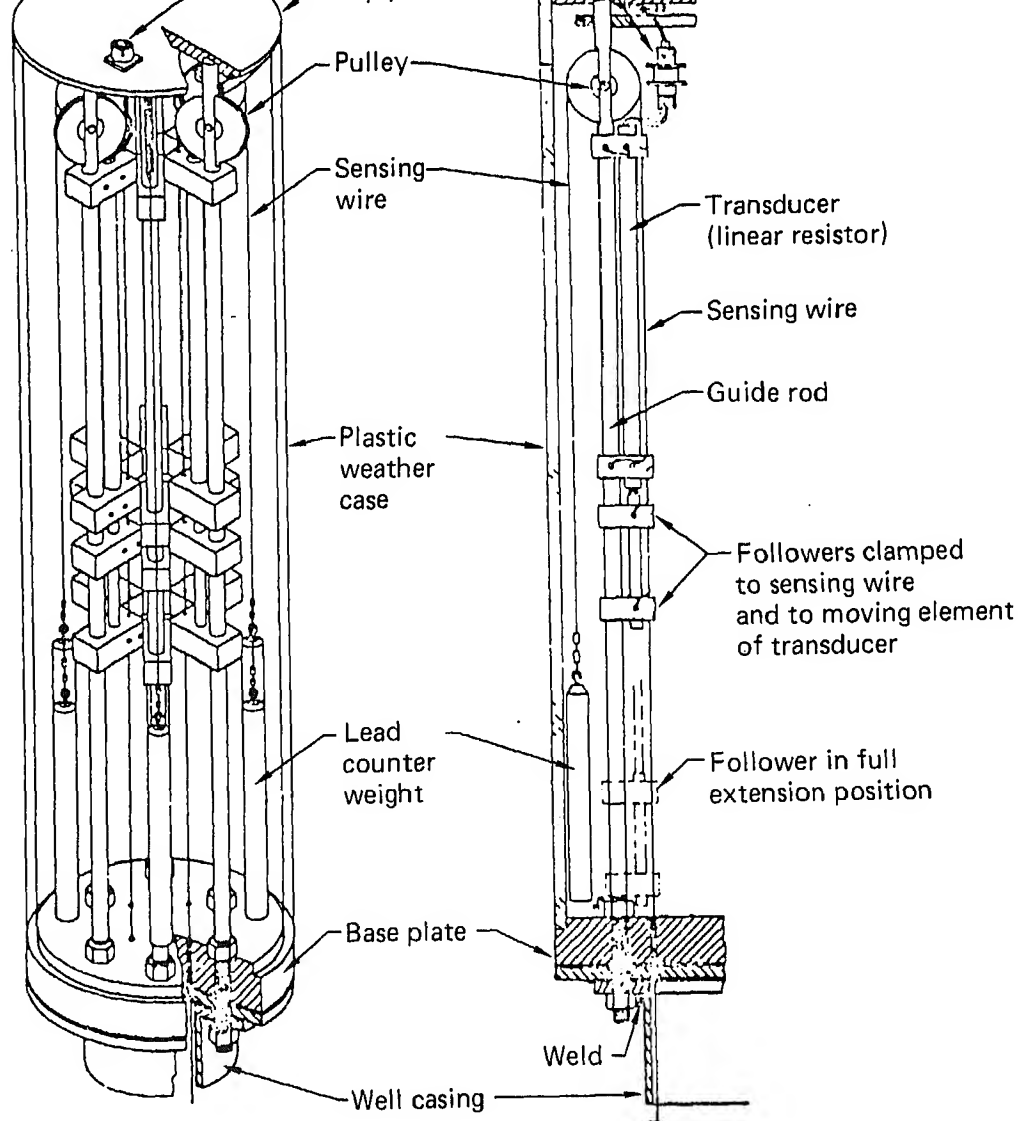


Figure 9. Multiple-position borehole extensometer sensing head. Cables from the sensing head extend down to expandable mechanical anchors located at various positions in the overburden. Displacements measured at the sensing head are the integrals of vertical strains occurring between the head and the various anchor points.

The usefulness of 3-dimensional solutions will also be explored. We are hopeful that an improved knowledge of subsidence behavior in actual gasification experiments, used in conjunction with properly measured overburden characteristics, can permit the development of predictive modeling capabilities that will be a reliable guide to the subsidence phenomena that may accompany large scale in situ coal gasification.

#### ACKNOWLEDGMENTS

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## 1. INTRODUCTION

High temperature entrained flow coal gasifiers have a well-known advantage over lower temperature fixed-bed or stirred-bed gasifiers. This advantage is the marked reduction in tars, phenols, and other condensible hydrocarbons as gasifier by-products. For example, Lurgi fixed-bed gasifiers produce from 50-100 pounds of tar, 30-70 pounds of tar oil and naptha, and 8-12 pounds of phenols per ton of coal (1,2). Similar by-product compounds and yields have been reported for a fluidized bed gasifier operated by the Pittsburgh Energy Research Center (3). On the other hand, the Koppers-Totzek and Texaco High temperature entrained flow gasifiers are claimed to produce negligible amounts of tars and oils as by-products. The gas and water purification equipment is, therefore, less complicated and less expensive than that required for the Lurgi process. It was anticipated that more advanced high temperature entrained flow gasifiers would also have this advantage.

The experimental gasifier studied in this report is housed at the Eyring Research Institute in Provo, Utah. This gasifier is a pressurized, entrained-flow gasifier that has a capacity of ~50 pounds of coal per hour and has a downflow configuration with some similarity to an entrained flow gasifier operated by the Bureau of Mines during the period 1952-1963. It also has some similarity to the Texaco entrained flow gasifier configuration.

## 2. PROCEDURE

A diagram of the laboratory gasifier and the necessary coal feeding, gas cooling and cleaning, and ash handling equipment is shown in Figure 1. Pulverized coal from a pressurized feed hopper is fed to the gasifier entrained in a stream of recycle gas. The coal is rapidly mixed and reacted with a mixture of super-heated steam and oxygen. The reaction is carried out at pressures of 75 to 150 psig and gasifier outlet temperatures of 2300-2800°F. Residence times for gasification reactions are of the order of 0.1 second.

The gasifier products pass downward into a quench section where they are

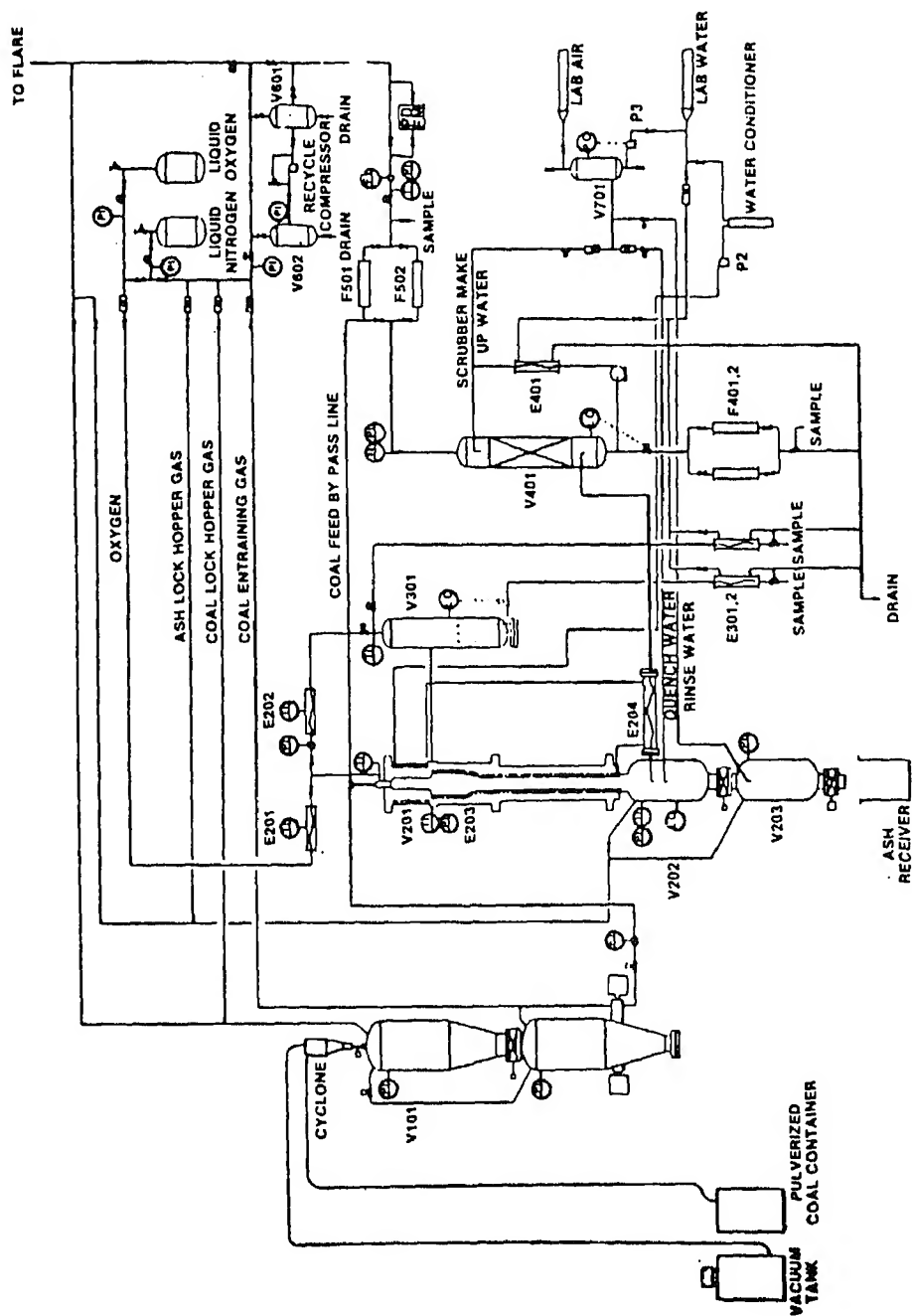


Fig. 1. Flow Diagram of Laboratory Scale Gasifier

V101	Coal lock vessel	18" × 57"
V102	Coal feed vessel	18" × 57"
V201	Gasifier section	10" × 12"
V202	Ash/slag accumulator vessel	10" × 4'
V203	Ash/slag lock hopper	10" × 3'
V301	Steam drum	4" × 4', 18 kw heater
V401	Scrubber column	10" × 4'
V601	Recycle gas inlet vessel	12" × 6'
V602	Recycle gas accumulator	14" × 6'
V701	H.P. water accumulator	10" × 3'
E201	Oxygen heater	3/8" × 40' coil, 5 kw
E202	Steam superheater	3/8" × 40' coil, 5 kw
E203	Steam evaporator	3/8" coil
E204	Economizer exchanger	19 tubes, 3/8" × 2'
E301,2	Condensers	5" × 24"
E401	Scrubber water cooler	60,000 BTUH
F401,2	Scrubber liquor filter	8" × 34", 4.4 sq. ft.
F501,2	Product gas filter	4" × 24"

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In this study, a detailed characterization of products and by-products associated with this gasifier was performed. Four process parameters, as shown in Table 1, were varied; coal feed rate, reactor pressure, oxygen to coal ratio, and steam to coal ratio. A high-volatile, non-caking, Utah bituminous coal was used for most of this study. A simplified flow chart showing the gasifier effluent streams is shown in Figure 2. Samples were taken from the cooled and water-scrubbed product gas stream, the scrubber effluent water, and the gas evolved on depressurization of the scrubber water. The gas samples were analyzed by gas chromatography and selective reaction indicator cartridges while the scrubber water was subjected to the analysis scheme shown in Figure 3. The scrubber water was first filtered to remove the particulate matter. Portions were then analyzed by proton induced x-ray emission (PIXE) and atomic absorption spectroscopy, thermometric titrimetry, and ion chromatography. Both the filtered scrubber water and the particulate matter were extracted with methylene chloride and analyzed by gas chromatographic mass spectrometry.

Table 1

Gasifier Test Parameters

Reactor Pressure (psia)	75	150	
Coal Feed Rate (lbs./hr.)	20	40	60
Oxygen to Coal Ratio (wt/wt)	0.8	0.9	1.0
Steam to Coal Ratio (wt/wt)	0.1	0.3	0.5

### 3. RESULTS

Analysis of effluent streams at median gasifier conditions. The data in Tables 2 through 5 represent the average of three gasifier test runs that were made under identical reactor conditions: coal feed rate = 40 lbs. of Utah bituminous coal/hour, reactor pressure = 150 psia, oxygen to coal ratio = 0.9, and steam to coal ratio = 0.3. Table 2 shows the product gas composition. Gases which were specifically tested for and not found at the sensitivity level of 0.5 ppm include  $\text{SO}_2$ ,  $\text{COS}$ ,  $\text{NH}_3$  and  $\text{CS}_2$ . The composition of the flash gas obtained during depressurization of the scrubber is given in Table 3. Again,  $\text{SO}_2$ ,  $\text{COS}$ ,  $\text{NH}_3$ , and  $\text{CS}_2$  were not detected.

Table 4 shows the net elemental composition of the scrubber water after subtraction of concentration levels measured in the water before scrubbing. PIXE analysis can detect nearly any element between atomic numbers 14 and 40 above an approximate detection limit of 0.5 ppm. The detection limits for heavier elements are somewhat higher. Notice that the data are given both in units of ppm in scrubber water and lbs per ton of coal feed. It was found impossible to compare our data with data from other gasifiers because of the inavailability of certain gasifier operating parameters.

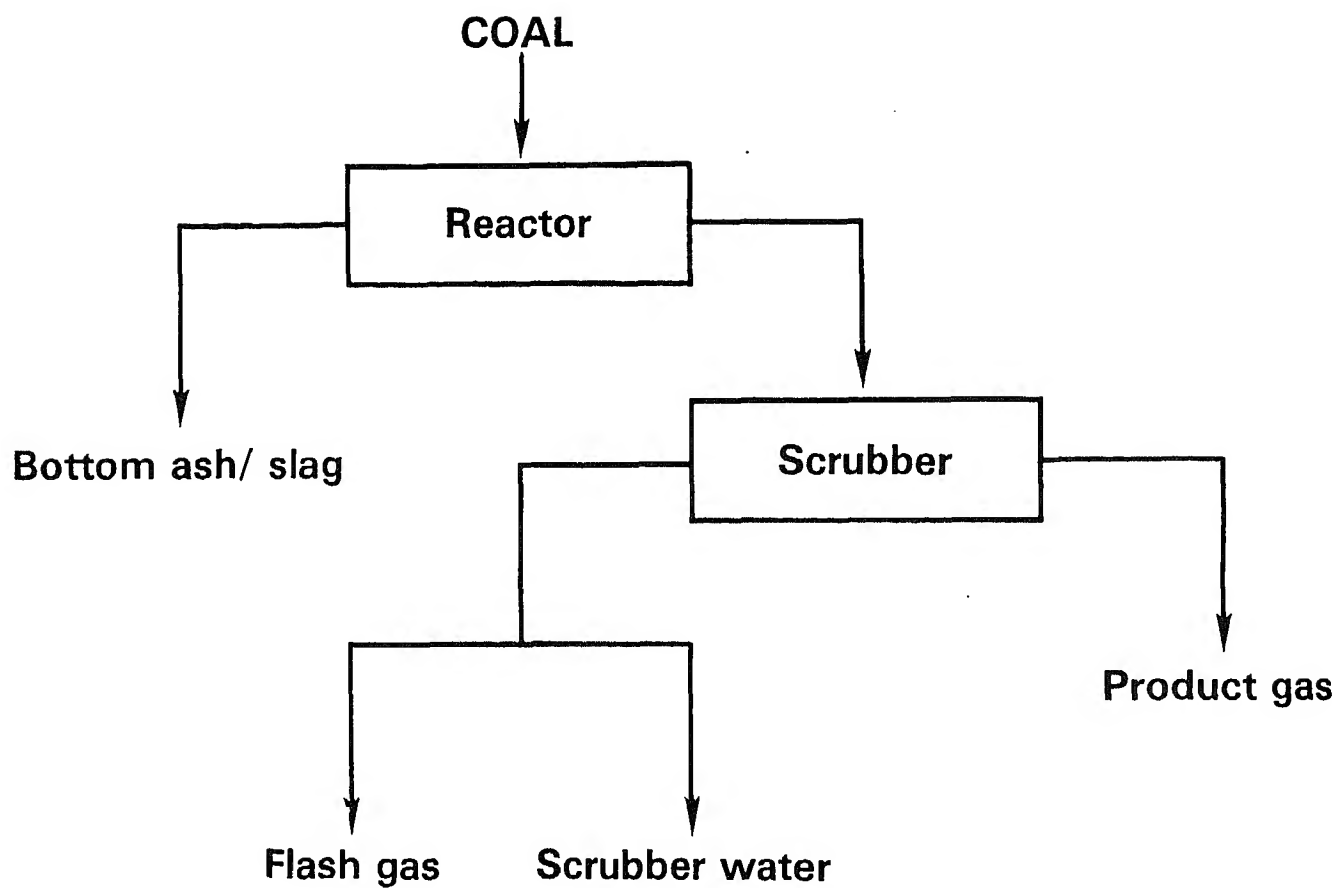


Fig. 2. Gasifier Product and Effluent Streams

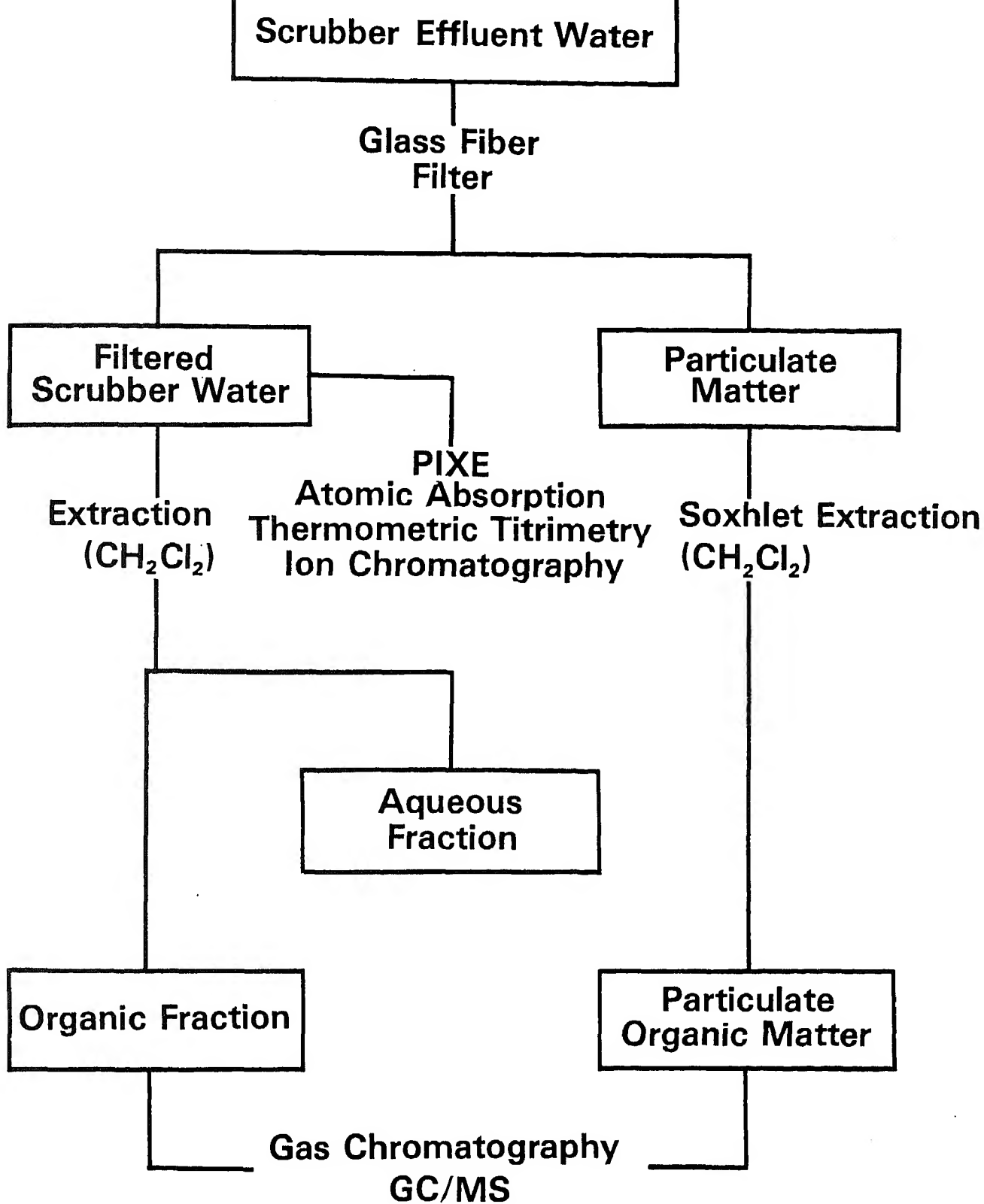


Fig. 3. Flow Diagram of Scrubber Water Analysis Procedure

CO	54%	2300	CO <sub>2</sub>	31%	14.0
H <sub>2</sub>	30%	88	N <sub>2</sub>	34%	9.9
CO <sub>2</sub>	11%	690	CO	31%	8.9
N <sub>2</sub>	5%	200	CH <sub>4</sub>	0.4%	0.6
CH <sub>4</sub>	0.7%	15	H <sub>2</sub> S	0.4%	0.14
H <sub>2</sub> S	550 ppm	3	H <sub>2</sub>	4%	0.007
HCN	1 ppm	0.004	HCN	44 ppm	0.001

Table 4

Filtered Scrubber Water Elemental Composition

Element	ppm	lbs/ton of Coal
Ca	50	4.6
S	8	0.78
Si	3	0.28
Fe	2	0.22
Cl	3	0.30
Zn	1	0.13
K	1	0.09
Sr	0.3	0.03

Cu, Ti, Mn, Ni, Br, Hg, Se, and As detected at same level both before and after scrubbing.

Other elements ( $14 \leq Z \leq 40$ ) not detected ( $<0.5$  ppm).

Table 5

Filtered Scrubber Water Inorganic Species

Species	ppm	lbs/ton of Coal
HCO <sub>3</sub> <sup>-</sup>	210	19.0
Cl <sup>-</sup>	9	0.85
F <sup>-</sup>	1	0.11
NH <sub>4</sub> <sup>+</sup>	45	4.12
NO <sub>3</sub> <sup>-</sup>	0.6	0.03

SO<sub>4</sub><sup>2-</sup> and SO<sub>3</sub><sup>2-</sup> detected at same level both before and after scrubbing.

Carboxylic acids, phenols, and amines not detected ( $<5$  ppm).

The reporting of data in terms of weight per weight or weight per volume of pollutant in scrubber water is important from an environmental standpoint, but nearly useless for quantitative gasifier production comparisons because of the variability in scrubber water flow rates. In fact, an effluent stream can appear to be quite clean when data is presented in terms of ppm, when in reality the seemingly low levels of pollutants are a direct result of a very fast scrubber water flow rate. For this reason, we report quantitative data both in

ion chromatography and thermometric titrimetry. Species not detected and approximate sensitivity levels are shown.

An interesting aspect of this study was the analysis of the organic compounds present in the scrubber water. After filtering 1.5 liters of the scrubber water through a  $1.2\mu$  pore filter, extracting 2 times with 100 ml each of methylene chloride, evaporating almost to dryness, and injecting the total amount into a gas chromatograph, essentially no organic compounds were found. On the other hand, the methylene chloride extract of the particulate matter which was filtered from the scrubber water contained significant amounts of organic compounds, all of which are polycyclic aromatic hydrocarbons. Figure 4 shows a capillary column gas chromatogram of the organic extract of the particulate matter of one sample. All peaks represent fused-ring aromatic systems. The absence of alkylated compounds is expected from a high temperature system.

There is only approximately  $1 \times 10^{-3}$  lbs. of extractable organic material in the unfiltered scrubber water per ton of coal consumed, and the total amount is quantitatively adsorbed on the particulate matter. Natusch (4) has recently presented a theoretical model describing the quantitative adsorption of polycyclic aromatic hydrocarbons onto fly ash due to the sudden decrease in temperature as the fly ash exits from the stack of a coal-fired power plant. It appears that the same process is occurring as the product gas stream is cooled by the spray of water in the scrubber column. We tested the adsorption of naphthalene on particulate matter in water by dissolving 15 mg of naphthalene in one liter of distilled water which was thermostated at  $22^{\circ}\text{C}$  and successively adding portions of previously extracted particulate matter. After each addition, the amount of naphthalene adsorbed was determined by UV absorption. Figure 5 shows the adsorption curve obtained. Notice that 100% adsorption will be obtained at approximately 0.40 ppt particulate matter in the water. Scrubber water from the gasifier typically contained about 2% particulate matter so there is clearly sufficient to adsorb all of the organics from the water.

From the data in Tables 2-5 it may be concluded that (1) the effluent streams from this type of gasifier are extremely clean when compared to other types of gasifiers, (2) all of the nonvolatile organic compounds produced are quantitatively adsorbed by the particulate matter in the scrubber water, and (3) the only potential pollutants from the gasifier other than the soot in the scrubber water and the bottom ash/slag are the  $\text{H}_2\text{S}$  and  $\text{HCN}$  in the product and flash gases and  $\text{NH}_4^+$  in the scrubber water. The  $\text{HCN}$  is present in such small amounts that it probably is not environmentally significant.

Effects of gasifier conditions on effluent streams. Table 6 summarizes the significant effects of changing the gasifier operating conditions. Decreasing the pressure in the gasifier from 150 psia to 75 psia decreased the CO output per ton of coal by a factor of about 1.5. This is a large loss of coal conversion efficiency. The output of  $\text{HCN}$ , polycyclic aromatic hydrocarbons as represented by naphthalene, and scrubber collected soot all increased.

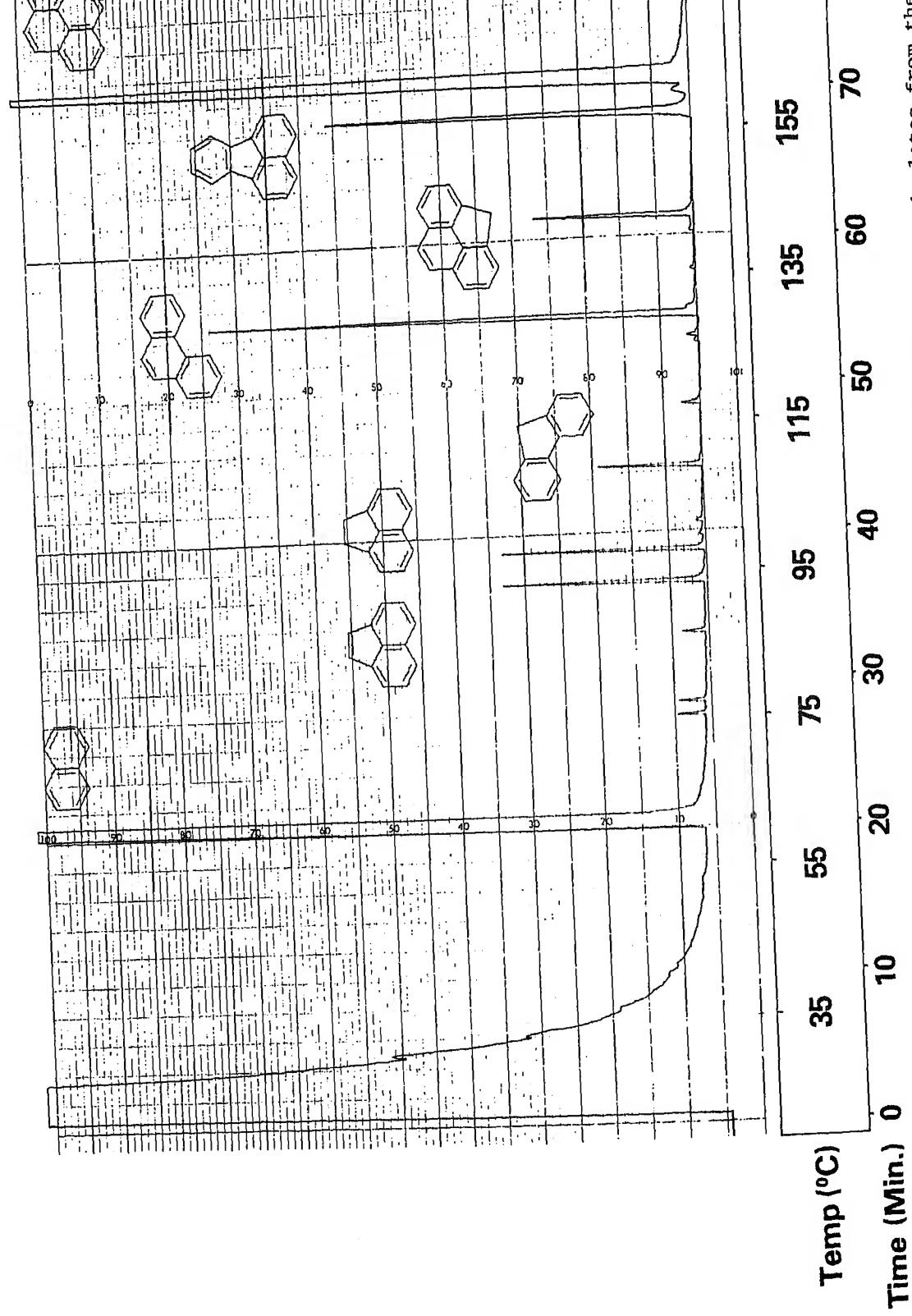


Fig. 4. GC Separation and MS Identification of Polycyclic Aromatics in Particulates from the water.

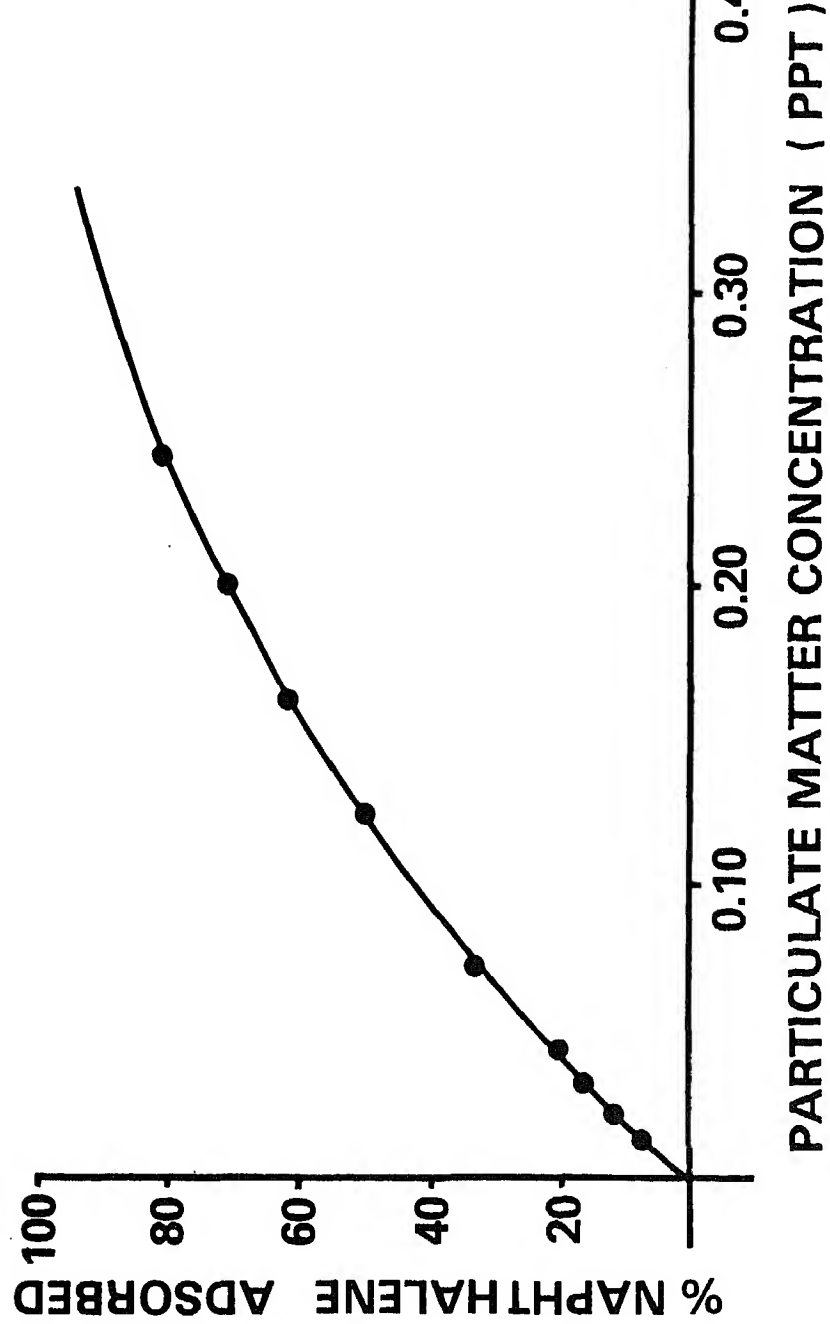


Fig. 5. Adsorption Isotherm for Naphthalene on Particulate Matter from the Scrubbers

Pressure 150 75 psia		Coal Feed Rate 60 → 40 → 20 1bs/hr	O <sub>2</sub> /Coal 1.0 → 0.9 → 0.8 1b/1b	Steam/Coal 0.5 → 0.3 → 0.1 1b/1b
<u>Product Gas</u>				
CO	decrease x 1.5 <sup>a</sup>	No effect then decrease x 1.8 <sup>a</sup>	c	c
H <sub>2</sub>	c	c	c	c
CH <sub>4</sub>	increase x 2 <sup>b</sup>	dec.-inc. x 4 <sup>b</sup>	increase x 4 <sup>a</sup>	c
H <sub>2</sub> S	c	c	decrease x 4 <sup>a</sup>	c
HCN	increase x 6 <sup>b</sup>	c	c	c
<u>Flash Gas</u>				
CO	c	c	c	c
H <sub>2</sub>	c	increase x 7 <sup>b</sup>	c	c
H <sub>2</sub> S	c	c	c	c
HCN	increase x 3 <sup>b</sup>	c	c	c
<u>Scrubber Water</u>				
NH <sub>4</sub> <sup>+</sup>	c	increase x 2 <sup>b</sup>	c	decrease x 2 <sup>b</sup>
Total naphthalene on soot increase x 7 <sup>a</sup>		decrease x 3 <sup>b</sup>	c	c
Soot increase x 4 <sup>a</sup>		decrease x 5 <sup>b</sup>	c	c

- a. Most significant changes.  
b. Not significant in comparison to other changes.  
c. No effect.

These results suggest that operating at pressures higher than 150 psia may result in better coal conversion efficiency and lower outputs of these pollutants. Attempts to run at higher pressures in the present gasifier resulted in mechanical problems, however.

Decreasing the coal feed rate below 40 lbs/hour also caused a large decrease in CO production. In this case production of naphthalene and soot were decreased.

Decreasing the O<sub>2</sub>/coal ratio in the reactor produced the only significant decrease in H<sub>2</sub>S found. Changing the O<sub>2</sub>/coal ratio from 1 (wt/wt) to 0.8 re-



In conclusion, higher pressures and lower  $O_2$ /coal ratios should be studied to see if the trends observed in this study continue to change with the gasifier parameters.

Sulfur chemistry. The whole question of the reactions of sulfur in the gasifier is an important area for further research. About 25% of the sulfur in the coal ends up as  $H_2S$  in the product and flash gases, another 10% ends up dissolved in the scrubber water as ionic species, and the remaining two-thirds of the sulfur is present in the bottom ash/slag and scrubber collected soot. The chemical state and fraction of the sulfur in the bottom ash/slag is unknown at present. The particulate sulfur collected in the scrubber is elemental sulfur which is tightly bound in the soot matrix. Sulfur was removed from the soot at a constant rate by Soxhlet extraction of the soot with  $CH_2Cl_2$  for several days. Such extractions never appeared to be complete.

The elemental sulfur in the soot is probably formed by oxidation of  $H_2S$  by oxygen containing groups on the surface of the graphitic soot particles. Similar behavior of activated charcoal which has been exposed to oxygen has been observed in other studies.<sup>5</sup> The presence of peroxides in the scrubber water was also inferred from the results of thermometric titrations of acidified scrubber water with  $Cr_2O_7^{2-}$ . An understanding of these reactions could lead to new methods for scrubbing  $H_2S$  from gas streams.

The soot produced in this gasifier and collected in the scrubber water thus serves two beneficial functions: (1) the quantitative removal of polycyclic aromatic hydrocarbons from the water and (2) the partial removal of  $H_2S$  from the product gas.

Gasification of other carbonaceous fuels. Preliminary experiments on other types of coal, lignite, and COED char indicate that gasifier conditions can be adjusted to gasify these fuels as cleanly as the bituminous coal.

## 5. CONCLUSION

If economical and simple means can be found to remove the residual  $H_2S$  from the product and flash gases and the soot from the scrubber water, this type of gasifier has the potential of supplying clean gas from coal with very little environmental impact on water or air quality.

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International Symposium on Polynuclear Aromatic Hydrocarbons, Columbus, Ohio, 1977.

- (5) D. J. Eatough, W. P. Green, and L. D. Hansen, "Oxidation of Sulfite by Activated Charcoal", Proceedings of a Conference on Carbonaceous Particles in the Atmosphere, Berkeley, Calif., 1978.

#### ACKNOWLEDGEMENT ,

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## INTRODUCTION

Increasing demands for natural gas and oil, partly caused by needs for environmental protection, have led to the inevitable situation where demand exceeds the U.S. productive capacity. The trade deficit from importing these clean fuels plus the uncertain political situation in the Middle East have prompted a drive for energy self-reliance in the United States.

Coal is a dirty, cumbersome fuel whose use in the past has been extensive, often with unfavorable consequences to the environment. Nevertheless, coal constitutes over 70% of the total estimated ultimately recoverable fossil fuel resources in the U.S. and will obviously be important in meeting future energy demands.

Besides being directly fired in boilers for generating steam to drive turbines and provide process heat, coal may be used for producing chemicals and clean fuels. Coal is used throughout the world as a raw material for synthesis of fertilizers and chemicals. This production generally uses a gasification system, such as Lurgi, Koppers-Totzek, or Winkler, to generate synthesis gas (usually hydrogen or a mixture of hydrogen and carbon monoxide).

Koppers-Totzek technology has had commercial application in at least 12 countries since 1955. The Texaco gasification process, which has been tested with coal at the semi-commercial scale and has operated commercially with oil in over 20 countries since the 1940's, is planned for commercial application in combined cycle power plants.<sup>1</sup>

Potential emissions from entrained flow coal gasifiers, such as the K-T and Texaco, are presented in this paper. Commercial control systems for treatment of potential emissions are discussed relative to their applicability to entrained flow gasifiers.

## DESCRIPTION OF GASIFICATION TECHNOLOGIES

Commercial, or near commercial, coal gasifiers that employ an entrained flow contacting method include the Koppers-Totzek (K-T) gasifier, the pressurized K-T, and the Texaco gasifier. Description of these gasifiers are presented in the following discussion.

years to produce liquid fuels from coal.

The first commercial plant employing Koppers-Totzek gasification was completed in Finland in 1952.<sup>2</sup> Since that time, plants have been built in Spain, Japan, Belgium, Portugal, Greece, United Arab Republic, Thailand, East Germany, Turkey, Zambia, and South Africa.<sup>2,3</sup> Plants at other locations are currently under construction.

The K-T process employs the partial oxidation of pulverized coal in suspension with oxygen and steam. The Koppers-Totzek gasifier, shown schematically in Figure 1, is a refractory-lined steel shell cooled with a steam jacket to produce low-pressure process steam. Coal, oxygen and steam are fed to the gasifier through opposing special metering heads or nozzles. Coal is pulverized to 70% through a 200 mesh screen and dried to from 2 to 8% moisture. Exothermic reactions create temperatures of 3300-3500°F at the gasifier outlet. About 50% of the ash is entrained with unburned carbon in the fuel gas while 50% flows down the refractory walls into a water quench at the base of the gasifier. Less than 2% of the coal carbon accompanies the ash streams. Flux is sometimes added to the coal to adjust ash fusion properties, such that the slag flows freely from the gasifier and does not solidify on the refractory wall.<sup>2,3</sup>

Two-headed K-T gasifiers with opposing nozzles 180° apart are capable of gasifying about 400 tons/day of coal to produce 15,000 scfm of gas. The capacity is essentially doubled in four-headed units with two sets of opposing nozzles 90° apart. The larger two-headed units are 10 to 12 ft in diameter, tapering to 6 to 8 ft at either end; overall vessel length is 25 ft. with an inner volume of about 1000 ft<sup>3</sup>. Four-headed gasifiers have similar dimensions and double the inner volume.<sup>2,3</sup>

Operational experience has shown that the gasification reactions can be controlled by monitoring the CO<sub>2</sub> concentration in the product gas. The CO<sub>2</sub> level indicates the extent of chemical reaction, and controls are adjusted to maintain the CO<sub>2</sub> concentration within a preselected range. Typical results using a K-T gasifier are given in Table 1.

The flow diagram depicted in Figure 2 shows schematically equipment used for synthesis gas production. The fire-tube boiler is inclined from the exit of the radiant boiler to a venturi scrubber. High-pressure steam (up to 1500 psig) is generated in the boiler. The gas from the boiler passes to a two-stage venturi scrubbing system where the particulate level is reduced to 0.002 to 0.005 grains/scf.<sup>2</sup> Large particles (95% of total) are removed in the first fixed venturi. A second adjustable venturi scrubber removes 99% of the remaining particles. After particulate removal, the gas is cooled to about 95°F with water in a packed tower. As in early designs, the gas is then compressed for sulfur removal.

Cooling and scrub water are recycled in a circuit shown schematically in Figure 2. Slag quench water is cooled to prevent evaporation losses, and makeup for water lost with the slag is provided from the cooling and scrub water circuit. Makeup water for the system is added to the packed cooling tower.

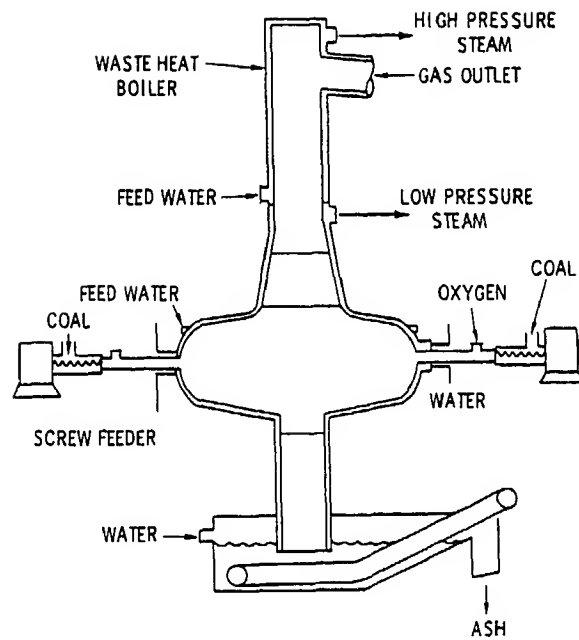


FIGURE 1. Koppers-Totzek Gasifier Schematic

TYPE OF FUEL	WESTERN COAL	EASTERN COAL	GREEN PETROLEUM COKE
<u>GASIFIER FEED</u>			
Dry Feed to Gasifier			
Analysis, Wt%			
C	72.7	69.9	88.0
H	5.3	4.9	4.5
N	1.1	1.3	1.4
S	1.0	1.1	4.3
O	9.0	7.1	1.0
Ash	8.9	13.7	0.2
Moisture	2.0	2.0	0.6
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>
Gross Heating Value of Dry Feed, Btu/Lb	13,135	12,640	15,690
Oxygen, Tons/Ton Dried Feed @ 98% Purity	0.878	0.849	0.950
Process Steam, Lb/Ton Dried Feed	814	810	1182
<u>GASIFIER PRODUCTS</u>			
Jacket Steam, Lb/Ton Dried Feed	600	554	629
High Pressure Steam, Lb/Ton Dried Feed @ 900°F/900 psig	2760	2675	3598
Raw Gas Analysis, Vol%, Dry			
CO	52.55	52.51	52.22
CO <sub>2</sub>	10.00	10.00	10.00
H <sub>2</sub>	36.09	35.96	35.40
N <sub>2</sub> + Argon	1.00	1.15	1.10
H <sub>2</sub> S	0.34	0.36	1.20
COS	0.02	0.02	0.08
	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>
Dry Gas Make - SCF/Ton Dried Feed	69,690	66,970	77,500
Gas Gross Heating Value, Btu/SCF, Dry	287	286	283
% Heating Value of Gas/Heating Value Feed (Gross Basis)	76.1	75.8	69.9

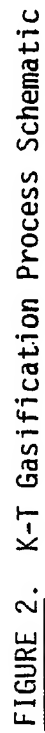


FIGURE 2. K-T Gasification Process Schematic

oxygen into the gasifier through special nozzles. The feed nozzles are arranged to inject the coal at velocities in excess of the flame propagation speed. The coal ash is completely liquefied in the flame zone, and about half of the ash in most coals drains from the bottom of the gasifier as molten slag into a quench tank. The remainder of the ash, which is entrained in the raw gas output, is generally solidified at the entry to the waste heat boiler beyond the gasifier by water spray injection to avoid ash adherence and build-up on the boiler surfaces.<sup>4</sup>

Problems have been encountered in some recent installations of atmospheric pressure Koppers-Totzek gasifiers due to the very low viscosity of the slag from certain feed coals at the 2200 K (3500°F) burner tip temperature. The Koppers-Totzek design depends on build-up slag on the ceramic lining of the reactors to protect the linings. Not only did such build-up not occur, due presumably to the very low viscosity of the slag, but there was apparently reaction and/or solution of the ceramic lining with the slag, resulting in rapid failure of the linings. Moreover, whereas about half of the slag from the lignite feeds (which are common to most of the sixteen Koppers-Totzek plants now operating around the world) would normally be expected to flow out of the bottom of the gasifier directly into an ash quencher, it was found that no more than about 5 to 10 percent of the slag could be recovered in this way. Most of the slag was going over into the waste heat boiler along with the gas, greatly overloading the ability of the design to handle the solidifying mixture.<sup>4</sup>

A partial solution to both of these problems has been to reduce the operating temperatures by increasing the steam-to oxygen ratio in the gasifiers. However, this has also decreased the carbon conversion efficiency to "somewhat below 90 percent."<sup>4</sup>

Koppers (U.S.A.) indicates that they have developed designs for pressurized gasifiers operating at 60 psi and at 1000 psi and are seeking an underwriter for the construction of one or both of these systems. Presumably, only very small-scale reactors have actually been operated at these pressures. The primary stumbling block to pressurized operation has been the development of reliable coal feed devices.<sup>4</sup>

Koppers (U.S.A.)<sup>4</sup> has reported that Shell (Dutch) and Koppers (Germany) have operated a 5 t/d pilot unit near Amsterdam for over two years. The plant has operated successfully on all ranks of coals at a pressure of 450 psi, producing a gas whose composition consisted of about 95 volume percent CO plus H<sub>2</sub>, 2.6% CO<sub>2</sub> and 0.3% CH<sub>4</sub>.

A 150 t/d unit constructed in Hamburg combines the experience of Koppers in the entrained bed gasification of solids at atmospheric pressure with Shell's experience on high pressure partial oxidation of liquids. The plant, which is highly proprietary, is expected to start operation by September 1978.<sup>a</sup> Koppers (U.S.A.) is not involved in the development of the process, but expects to be able to license the process. They expect no commercial conclusion to be drawn with regards to the process before 1983

a) Information received by telephone from Mr. James W. Bumbaugh, Koppers, Engineering and Construction Div., Koppers Company, Inc., Pittsburgh, PA, August 1978.



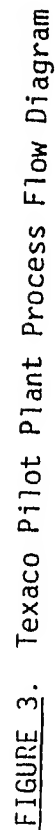
## TEXACO COAL GASIFIER

The Texaco gasifier was developed by Texaco, Inc. at their Montebello Research Laboratory in California during the 1940's. It was routinely operated from 1946 through 1954 to provide synthesis gas for an on-site pilot plant that was a modification of the Fischer-Tropsch process.<sup>5</sup> Since 1953, the Texaco process has been in commercial use for the production of synthesis gas from petroleum feedstocks and is currently used in approximately 70 plants in over 20 countries.<sup>6,7</sup> The process, which was initially developed for the partial oxidation of natural gas, has developed the versatility to use light oils, residual oil, petroleum distillates, asphalt, heavy oils, or coal as feedstocks. The Texaco process is the only high pressure suspension gasification process that has been operated on an industrial scale. Most of this experience has been with heavy oil as feedstock and dates back to 1953.

The Texaco gasifier is a vertical cylindrical pressure vessel (up to 85 atm) with a carbon-steel shell, the top section where gasification occurs is refractory lined. The lower section (slag quench chamber), which contains a reservoir of water for the quenching of gas, is unlined steel.<sup>6</sup>

Process flow diagram of the Texaco coal gasification pilot plant is shown in Figure 3. In the process coal, which has been ground to pass through a 40-mesh screen, is mixed with water in a slurry mix tank. The resultant slurry containing about 40 to 60 wt.% coal is pumped through an optional preheater to a temperature of 700-1000°F or more. The coal particle size has been reported to be reduced further in this heating coil, either as a result of attrition or as a result of the rapid expansion of water undergoing evaporation.<sup>5</sup> Since the proportion of water required to slurry and pump the coal was greater than that required for efficient gasification, up to 75 percent of the steam is separated in a cyclone in front of the gasifier.

The coal feed slurry enters the reactor either axially at the top or tangentially near the top through a water-cooled burner nozzle of proprietary design. Preheated oxygen is fed through a separate water-cooled nozzle oriented to prevent impingement of oxygen on the wall of the reactor.<sup>8</sup> Slag flows through a constricted opening at the bottom of the reactor into a quench tank and becomes granulated. The granulated slag, which is heavier than water and which generally contains less than one percent carbon by weight, is removed periodically from the bottom of the quench chamber by a lockhopper system. The fine solids, or soot, which are lighter than slag and which are principally ungasified carbon, are continuously removed from the quench section as an aqueous slurry. These solids are concentrated in a settling system and may be returned to the slurry preparation system if desired. Since the settling system operates at near-atmospheric pressure, flash gases are evolved with pressure letdown. The gases are reportedly very similar in composition to the product gas, except for a higher percentage of CO<sub>2</sub> and H<sub>2</sub>S.<sup>5</sup> If the clarified water from the settling system is recycled to the quench chamber and scrubbing section, a blowdown stream is required to maintain the total dissolved solids at a desired level.<sup>5</sup> This stream reportedly contains no tars or phenols. The quenched product gas can be treated in an acid gas removal system.



plant so that its performance can be studied.<sup>9</sup>

The pilot Texaco gasifier at Montebello operates at pressures up to 350 psig and has a reaction volume of about two cubic feet. The temperature in the reaction zone ranges from 2000 to 2500°F. Throughputs of 1000 lb/hr of coal have been reported. Carbon conversions are primarily controlled by the amount of oxidant fed to the system, and are typically above 90 percent on a single pass basis. Only limited performance data have been reported<sup>10</sup> with carbon conversions between 90 to 98%, thermal efficiency ranging from 75 to 80% and oxygen requirements of 350 to 375 scf/Mcf of make gas. The gas contained about 8% CO<sub>2</sub>, 1% CH<sub>4</sub>, and had a H<sub>2</sub>/CO ratio of about one. It has also been reported that, the oxygen consumption rates ultimately expected are 15,000 to 20,000 scf per ton of dry coal with 80 to 90% of the heating value of the coal appearing in the form of hydrogen and carbon monoxide in the synthesis gas.

Very limited operating details and results using coal have been published for the Texaco process. Table 2 lists some typical results for gas, fuel oil, and coal firing.<sup>5</sup> It should be noted that at least for fuel oil operations the distribution of sulfur compounds in the product gas was very similar to that calculated for equilibrium. As an example, Texaco cited a study in which the observed sulfur distribution as hydrogen sulfide, carbonyl sulfide, and carbon disulfide was 89, 11, and 0.03 percent, respectively; and the calculated equilibrium distribution was 93, 7, and 0.05 percent, respectively.<sup>11</sup>

### COMMERCIAL CONTROL SYSTEMS

The gasification of coal in an entrained flow system involves a number of processing steps. The steps in the direct process include coal storage, coal preparation, gasification, gas quenching, particulate removal and acid-gas removal. End use of the gas will determine if further gas processing, such as shift conversion, is required. In addition to the steps in the direct process, auxiliary facilities are required and usually include an oxygen plant, a sulfur plant, a utility boiler, raw water and waste water treatment facilities, and cooling towers.

The complexity of the multi-step process for coal gasification increases the difficulty of controlling environmental pollutants. All aspects of the conversion process, from coal storage to final product, require extensive study to assess the potential for pollutant emissions, determine actual emissions, and proceed to a control strategy which is technically and economically effective.

Figure 4 presents a simplified schematic of the overall process and delineates possible effluents from each processing step, excluding the mining operation. Each operation involved in the conversion process, from coal storage through final gas utilization, is a potential source of environmental pollution. Effluents from auxiliary facilities should also be considered.

The following discussion relates to the operations that are somewhat unique to an entrained flow gasification process. Operations such as coal storage, coal preparation, oxygen production, and the utility boiler are

Fuel Type Fuel Composition, Wt. %	Natural Gas	Fuel Oil	Pittsburgh Coal	Japanese Coal
C	74.42	85.59	77.3	64.3
H	21.94	11.38	5.3	4.9
O	1.67	0.35	5.2	15.0
N	1.98	0.72	1.4	0.9
S	-	1.96	2.5	1.8
Ash	-	-	7.1	13.1
Moisture	-	-	1.2	-
Fuel Rate, lb/hr	1714	429	-	-
Oxygen/Fuel, lb/lb	1.30	1.02	0.84	0.66
Steam/Fuel, lb/lb	-	0.38	0.70	0.67
Gas Composition, Mole % (dry)				
CO	38.02	47.97	46.6	45.7
CO <sub>2</sub>	2.19	3.65	11.5	13.2
H <sub>2</sub>	59.54	47.45	38.7	37.9
CH <sub>4</sub>	-	0.44	0.7	0.6
N <sub>2</sub>	0.15	0.22	2.0	1.7
H <sub>2</sub> S	-	0.02	-	-
COS	-	0.02	-	-
Gas Yield, scf(dry)/lb fuel	58.38	50.36	38.31	31.06
Materials per 1000 scf (CO + H <sub>2</sub> )				
Fuel, lb	17.6	20.8	30.6	38.5
Oxygen, scf	271.7	252.3	306	302
Steam, lb	-	7.9	21.5	25.8
Carbon Conversion, %	100	96.6*	92.1*	91.3*

\*Calculated from reported data

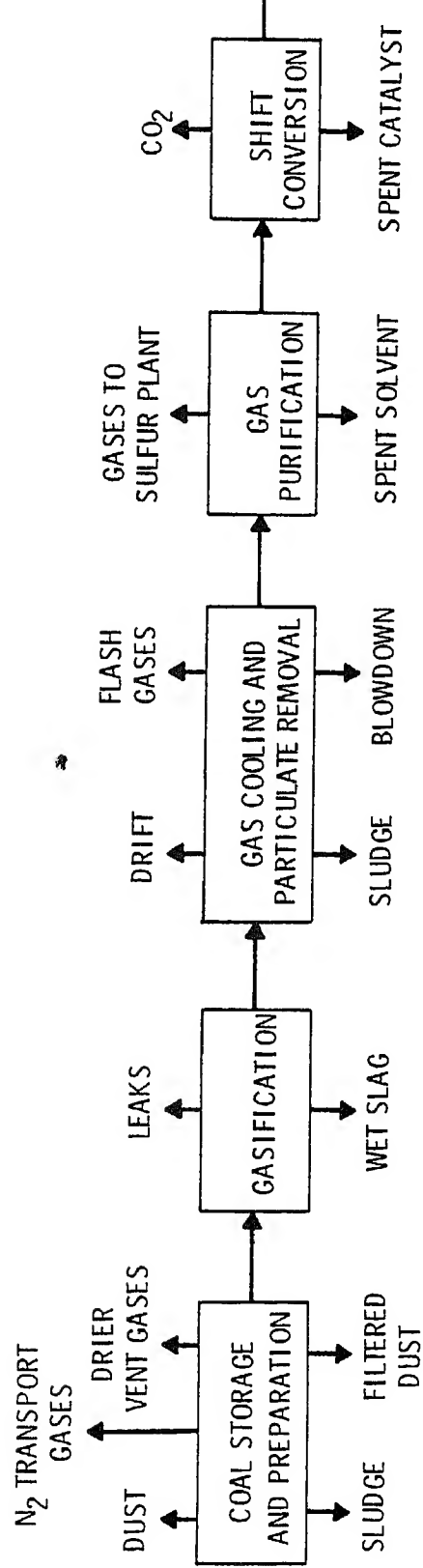


FIGURE 4. Effluent Streams From Coal Gasification

## GASIFIER OPERATIONS AND PARTICULATE REMOVAL

The objective of gasifier operations for the K-T and Texaco processes is to react coal with oxygen and steam to produce a synthesis gas consisting of  $H_2$  and CO accompanied by varying amounts of  $CH_4$ . During gasification other gases are produced, including  $CO_2$ ,  $N_2$ ,  $H_2S$ , COS, and  $C_2H_6$ . Of these gases the sulfur compounds are of major consequence. Other potential pollutants may also be generated: tars, oils, phenols, ammonia, particulates, other organic material, and trace elements.

Although gaseous pollutants are produced in the gasifier, these are not of immediate environmental concern as they are contained in the raw gas leaving the gasifier and are treated in subsequent process treatment steps. Exceptions are emissions due to leaks in gasifier seals and in pressurized lock hoppers and other feeding systems. These leaks would allow gaseous pollutants to escape directly into the atmosphere and would be significant sources of pollution. This situation would require immediate correction.

Contaminated water streams appear to be the major potential source of pollution from the gasifier, gas cooling, and particulate removal systems. Solid residues in the form of ash, slag, soot and sludge will require land disposal. These solid residues will contain inorganic ashes, metals, and unreacted carbonaceous matter of unknown composition that may prove to be of consequence. At present most gasification schemes use mine backfill or landfill as the method of disposal for this material. This method of disposal may prove to be environmentally unsatisfactory for some wastes, especially ash residues that have a high potential for leachability. This problem can only be evaluated after complete analysis of specific gasifier waste streams.

Reaction zone temperatures in entrained flow gasifiers are necessarily high to achieve adequate conversion with a short residence time. Temperatures are in the range of 3300 to 3500°F in the K-T gasifier and 2000 to 2500°F in the Texaco gasifier. The product gas, therefore, contains no condensible hydrocarbons. No phenols, pyridines, or organics are produced. However, ammonia and cyanide are present in the K-T product gas. Gas analyses before and after particulate removal for a K-T system are shown in Table 3.<sup>12</sup> The analyses shown in Table 3 represent operating data from a plant using a primary and secondary venturi scrubber in which the gas is intimately contacted with recirculated water.

### Discharges to Air

In the atmospheric pressure K-T system, discharges to the air could result from stripping the components dissolved in scrub water and direct contact cooling water by air in the cooling tower (see Figure 2). No further discharges to the air environment are foreseen since the product gas from particulate removal is compressed and passed to the acid gas removal system for further processing.

As shown in Table 3, some components are retained in the scrub water and cooling water.<sup>12</sup> All concentrations after particulate removal should increase by a factor of 1.3 over concentrations before removal because of the decrease in  $H_2O$  concentration resulting from condensation. Components retained in the scrub water are COS, HCN,  $SO_2$  and NO. These could be stripped by direct contact cooling of the scrub water.

TABLE 3. K- Gas Analysis

Component	Volume Percent	
	Before Particulate Removal	After Particulate Removal
CO	37.36	49.50
CO <sub>2</sub>	7.13	9.42
CH <sub>4</sub>	0.08	0.11
H <sub>2</sub>	25.17	33.35
N <sub>2</sub>	0.30	0.40
H <sub>2</sub> S	0.23	0.3
COS	178 ppmv	15 ppmv
HCN	288 ppmv	300 ppmv
NH <sub>3</sub>	0.17	0.22
H <sub>2</sub> O	29.19	6.20
Ar	0.32	0.42
SO <sub>2</sub>	22 ppmv	15 ppmv
NO	7 ppmv	7 ppmv
Particulates (grains/scf)	11.57	0.002

In the Texaco system, possible contamination of the air environment could result from combustion of gases from the flash drum, see Figure 3. These gases are flashed from scrub water and quench water solutions after pressure letdown in the flash drum. These gases will probably have a composition similar to the product gas but richer in components such as CO<sub>2</sub>, H<sub>2</sub>S, COS, SO<sub>2</sub> and NO. This stream may require treatment before it can be flared.

#### Discharges to Water

In commercial K-T plants, the reduction in particulate concentration shown in Table 3 is accomplished in the washer cooler, venturi scrubbers and separator. About 50% of the ash content in the coal leaves the gasifier as a slag quenched in water at the base of the gasifier.

Water flow in the cooling and scrubbing system proposed for U.S. applications is shown in Figure 2. Solids retained in the water are removed in a clarifier. If water is not a premium consideration, a slurry can be pumped to a disposal area. Water conservation can be effected by filtering the slurry, returning the water to the circulating system, and disposing the filter cake by truck or railroad car transfer to the worked-out mine or disposal area. Since all the particulate matter is slagged in the gasification process, leachable contamination should be low. Water loss with the ash may serve as blowdown for the cooling towers.

Analyses of water from the various cleaning and cooling stages in the Kutahya, Turkey, plant are shown in Table 4.<sup>12</sup> This table shows the level of water contamination that occurs in commercial practice. Not all trace element concentrations are noted in Table 4; proposed drinking water standards, EPA 1975 limits, are 0.2 mg/l for cyanide.

TABLE 4. Process Water Analyses from Koppers-Totzek Gasification

Property	S	Sample Location				
		1	2	3	4	5
pH		8.8	8.8	8.9	7.5	8.8
Conductivity		$7.6 \times 10^{-4}$	$1.8 \times 10^{-3}$	$2.0 \times 10^{-3}$	$9.7 \times 10^{-4}$	$1.8 \times 10^{-3}$
CaO	mg/l	78	101	78	85	135
MgO	mg/l	97	161	194	102	145
Na	mg/l	17.5	17.5	17.5	17.5	17.5
K	mg/l	5.6	8.8	10	6.8	8.0
Zn	mg/l	0.01	0.03	0.02	0.03	0.02
Fe	mg/l	0.05	0.22	1.95	0.26	0.64
NH <sub>4</sub>	mg/l	0.32	157	184	25	122
NO <sub>2</sub>	mg/l	0.02	0.13	4.47	5.34	4.37
NO <sub>3</sub>	mg/l	58.2	3.32	13.7	34.0	22.9
PO <sub>4</sub> Total	mg/l	1.89	0.81	1.21	1.69	2.70
Cl	mg/l	18	85	96	53	46
SO <sub>4</sub>	mg/l	42	216	155	147	109
CN	mg/l	0.26	0.52	12.5	7.0	1.4
H <sub>2</sub> S	mg/l				not detected	
KMnO <sub>4</sub> Consumed	mg/l	8	9	400	14	11
COD	mg O <sub>2</sub> /l	14	18	128	18	16
SiO <sub>2</sub>	mg/l	14.8	16.0	14.8	30.6	19.8
Suspended Solids	mg/l	14	4612	5184	278	3072
Cu	mg/l	0.01	0.01	0.01	0.06	0.01

- 1) Cooling water to gasifier seal pot.
- 2) Water from gasifier seal pot.
- 3) Wash water after washer-cooler.
- 4) Wash water after Theisen washer.
- 5) Water into clarifier.
- 6) Water out of clarifier.
- 7) Water out of cooling tower.



scrubber cooling tower blowdown and drift loss) shown in Table 4. Drift loss from the scrubber cooling tower (16,220 lb/hr drift loss with coal feed rate of 562,500 lb/hr, 8,830 BTU/lb, from Reference 14) with the composition shown in Column 7 of Table 4 are included in Column 3 of Table 5 for comparison of releases to the standards even though drift losses are not a direct water discharge. Releases from drift loss approach the standards and indicate that water releases must be minimized, or waste water must be treated prior to release.

It may be necessary to steam strip gaseous components such as  $\text{NH}_3$ ,  $\text{SO}_2$ , and HCN from the clarifier water before it passes to the cooling tower to prevent their being stripped by direct contact with air. Koppers proposes to remove a bleed stream from the recirculated water system to a steam stripper. Gaseous  $\text{NH}_3$ ,  $\text{SO}_2$ , and HCN flow to a Claus unit and are combusted while the stripped water is cooled and returned to the circulating system.

Considerations for the pressurized K-T and Texaco systems are similar to those for the K-T system. Water for gas cooling and scrubbing can be treated and recycled. Water streams from the Texaco process that must be treated include water from the slag quench chamber in the lower half of the gasifier unit, gas quenching liquor and process condensate, and clarifier water.

TABLE 5. Adjusted New Source Performance Standards  
(pounds of pollutant per  $10^{12}$  BTU feedstock, 30 day maximum)<sup>(a)</sup>

<u>Pollutant</u>	<u>Petroleum Refineries</u>	<u>Coke Making</u>	<u>K-T Drift Loss Estimate</u>
BOD	230-1015	477	200 (COD)
TSS	143-646	242	190
Ammonia (as N)	46-400	242	180
Oil and Grease	71-233	12	-
Phenols	1.5-7.1	5.8	-
Sulfide	1.2-5.8		

(a) Assumes heating values of 6.5 mm BTU/bbl of crude oil and 12,000 BTU/lb of coal, with a coke yield of 0.69 lb coke/lb coal.

system. Quench water, which contains dissolved matter, is drawn off near the bottom of the quench chamber and sent to a clarifier. No quantitative information is available on the characteristics of this stream; however, it is expected that the water will contain components such as shown in Table 4. Scrubber water (process gas condensate) from the scrubber knock-out pot is also sent to the clarifier. This stream is expected to contain suspended coal fines and slag,  $\text{CN}^-$ ,  $\text{S}^{2-}$ , ammonia, trace elements and organics.<sup>15</sup>

Water from the clarifier in the Texaco System is circulated to the flash drum where flash gas is vented to a flare. Make-up water is added to the clarified water in the flash drum and the water is recycled to the quench chamber.

#### Discharges to Land

Sludge from the clarifier and slag from the quench system for entrained flow gasifiers are usually sent to landfill. The sludge may be dewatered by filtration either before or after transport to a disposal site. Since all the solids have been slagged, very little leaching to ground water should result. The water associated with the slag and sludge will have the compositions shown in Table 4, columns 2 and 6 respectively.

Ash from the clarifier and slag quench system could have properties that significantly differ from power plant fly ash.<sup>16,17,18,19</sup> Ash from gasification processes is exposed to a reducing atmosphere, and elements may exist in a reduced form. Trace metals may be more soluble than fly ash trace elements in a number of water streams. This is likely to change effluent loadings to the waste water treatment facilities and, therefore, require alternative water treatment techniques. Furthermore, a change in solubility may affect the leachability of inorganic compounds present in the final slag to be disposed and runoff from disposal areas will have to be monitored until firm data is established. Koppers-Totzek has reported data on major components in some of their water streams (see Table 4), but no data are available on trace elements. No information on trace elements is available on slag quench, sluice, or elutriation waters. From the water analyses in Table 4 it is apparent that the ash from Kutahya plant would render the soil basic. Unlike mine refuse and coal preparation refuse, the residue from gasification does not contain sulfur (pyrite) which causes the acid mine drainage problem.

Discharges to land from entrained flow gasifiers is predicted not to cause any environmental problems. Since the ash has been slagged, dust problems from disposal sites should be minimal. Disposal sites should be monitored to characterize runoff streams.

#### ACID GAS REMOVAL

The removal of contaminants, especially sulfur, is a critical part of the gasification of coal. Contaminants that could potentially be present in the impure gas from entrained flow gasifiers consist of sulfur in the form of  $\text{H}_2\text{S}$ ,  $\text{COS}$ ,  $\text{SO}_2$ , and organic sulfur compounds, as well as nitrogen oxides, ammonia, cyanides, pyridines, hydrocarbons, odors, trace elements (Pb, Se, As, Te, F, Hg, Ga, Ge, Cd) that volatilize at gasification temperatures, and particulates. Gases from entrained flow systems are usually very low in hydrocarbons because of high reaction zone temperatures.

of reducing sulfur content in the gas to 0.1 ppm to 5 ppm. Carbon dioxide is also selectively removed in these processes along with the sulfur gases.

Other processes have been proposed for the removal of acid gases. One of these is the Benfield Hot Carbonate Gas Purification process followed by sponge iron and activated carbon traps, as proposed for the Synthane process. Koppers-Totzek processes will use one of the three already mentioned processes, while proposed Lurgi gasification facilities will use the Rectisol process or the Stretford process for  $H_2S$  removal.

Commercial processes for removal of sulfur gases are listed in Table 6.<sup>20, 21</sup> These processes are usually insensitive to pressure, high pressure operation being preferred. The efficiency of these processes for removal of  $H_2S$  is dependent on the concentration in the gas to be treated, but usually about 99% of the  $H_2S$  is removed. Regeneration of the solvent is accomplished thermally or with steam. In the chemical solvent and physical solvent processes, the  $H_2S$  stream from regeneration is usually sent to a Claus plant where it is converted to elemental sulfur. In the direct conversion and drybed processes, regeneration produces elemental sulfur directly.

#### Discharges to Air

Gas purification has several potential release areas. A scrubbing system that uses a solvent must periodically dispose of spent solvent or regenerate it in some manner; either alternative could cause environmental problems. The extent of this disposal problem is dependent on the lifetime of the solvent and characteristics of the contaminants. If the  $H_2S$  containing stream is not oxidized in a Claus plant, another problem may arise. This problem involves traces of other components, such as  $NH_3$ ,  $CO_2$ , or light hydrocarbons, that may be present along with the  $H_2S$ . These compounds may go through the sulfur production step unaffected, or may interfere with the sulfur recovery process.

#### Discharges to Water

Removal systems can be designed to reduce liquid effluents to zero pollutants.<sup>12</sup> Purge streams are usually incinerated to eliminate discharges to water. Alternatively, depleted solution may be sent to waste water treatment.

#### Discharges to Land

No solid effluent streams are encountered in acid gas removal. Elemental sulfur is produced in the Claus plant.

### AUXILIARY FACILITIES

Facilities not directly in the process flow include the oxygen plant, sulfur plant, waste water treatment plant, makeup water treatment plant, the cooling tower, and the utility boiler. Some of these auxiliaries are needed to treat effluents from the main process.

The auxiliary facilities represent well-developed technologies that have been in commercial use for many years. In most cases, their application to entrained flow gasification processes, such as the Texaco and K-T, is not unique. Possible exceptions include the sulfur plant (Claus plant) and the waste water treatment plant.

<u>Process</u>	<u>Absorbent</u>	<u>Type of Absorbent</u>	<u>Temp. °F</u>
Chemical Solvent type:			
MEA	Monoethanolamine	Aqueous solution	80 to 120
DEA	Diethanolamine	Aqueous solution	100 to 130
TEA	Triethanolamine	Aqueous solution	100 to 150
Alkazid	Potassium dimethylamino acetate	Aqueous solution	70 to 120
Benfield	Activated potassium carbonate solution	Aqueous solution	150 to 250
Catacarb	Activated potassium carbonate solution	Aqueous solution	150 to 250
Physical solvent type:			
Sulfinol	Sulfolane + Diisopropanomine	Organic solvent	80 to 120
Selexol	Polyethylene glycol ether	Organic solvent	20 to 80
Rectisol	Methanol	Organic solvent	<0
Direct Conversion:			
Stretford	Na <sub>2</sub> CO <sub>3</sub> + anthraquinone sulfonic acid	Alkaline solution	
Drybed type:			
Iron Sponge	Hydrated Fe <sub>2</sub> O <sub>2</sub>	Fixed bed	70 to 100

to process stripped gases with a high CO<sub>2</sub> content relative to H<sub>2</sub>S. Efficiency of sulfur recovery decreases as the inlet concentration of H<sub>2</sub>S to a Claus plant decreases. An inlet concentration of over 20 volume % H<sub>2</sub>S is desirable. The presence of CO<sub>2</sub> in high concentration can also present problems by reacting with H<sub>2</sub>S to form COS. With the availability of Claus tail gas cleaning processes, adequate commercial technology for sulfur control is available for use with entrained flow systems. Sulfur recovery in the form of sulfuric acid and elemental sulfur is being practiced at K-T installations throughout the world.

Applicable commercial processing steps for waste water treatment include stripping for removal of dissolved gases (H<sub>2</sub>S, NH<sub>3</sub>, CO<sub>2</sub>), clarification for removal of suspended solids, biological oxidation, and sand filtration. The main waste water sources are the slag quench water, particulate scrub water, and spent solvent solution. Waste waters from entrained flow systems will be low in dissolved organics since the high gasification temperatures destroy heavy organics. The low organic content should simplify waste water treatment.

### ENERGY REQUIREMENTS

The environmental impact of an operation can be related directly to the energy used for that operation. It is, therefore, extremely important to determine the areas in a system that require large amounts of energy.

Energy requirements for different operations employed in the K-T gasification process were determined from literature sources and are tabulated in Table 7. Sources of information are referenced in the table.

TABLE 7. Process Energy Requirements

<u>Operation</u>	<u>Required Energy, % of Gasifier Input</u> <u>Koppers-Totzek</u>
Coal Preparation (drying and grinding)	6.3 <sup>(a)</sup>
Particulate Removal	<1 <sup>(b)</sup>
Compression	15.4 <sup>(a)</sup> (7.2) <sup>(c)</sup>
Acid Gas Removal	4 - 7 <sup>(d)</sup>
Oxygen Plant	11.1 <sup>(e)</sup> (16.9) <sup>(a)</sup>
Sulfur Plant	--
Tail Gas Cleanup	0.1 <sup>(f)</sup>
Cooling Water Pumps, Air Fans	1.8 <sup>(a)</sup>

- (a) Data from Reference 14, calculated as described above.
- (b) Data from Reference 22, pp. 20-100 to 20-108.
- (c) Adiabatic compression to 165 psig.
- (d) Data from Reference 23.
- (e) Data from Reference 20, p. 14.
- (f) Data from Reference 24.

pound of steam was considered to cost 1500 BTU of fossil energy and 10,000 BTU of fossil energy produced 1 kWh of electricity.

Generation of the oxygen required for coal gasification and gas compression are the major users of energy in the gasification systems. Coal preparation (mainly drying) and acid gas removal are also large users of energy. Examination of process improvements in these areas, therefore, have the greatest potential for energy savings. Decreasing energy demand will benefit the environment in direct proportion to energy savings. However, the areas represented as large energy users represent highly developed technology. It is unlikely, for example, that significant energy saving improvements in oxygen plant operation can be expected. Acid gas removal processes can be selected on the basis of their energy requirement, e.g. steam requirements for solvent regeneration vary significantly for different processes.<sup>23</sup>

### CONCLUSIONS

Several conclusions may be drawn from this study:

1. Coal storage, preparation and drying processes are commercially available. Coal storage and handling methods used by coal-fired power plants should be directly applicable to gasification using Koppers-Totzek and Texaco gasifiers. Crushing and drying requirements for gasification are somewhat more severe than those encountered by coal-fired power plants.
2. Sulfur and particulates are completely removed from the product gas in the commercial operations as required for use of the gas for chemical synthesis. These systems have been in use for over 40 years. Claus plants are employed in some of these commercial operations to convert the sulfur compounds to environmentally acceptable elemental sulfur. Reduced  $H_2S$  concentration in stripped gases to the Claus plant will reduce efficiency for sulfur recovery.
3. Tail-gas cleanup processes for reduction of Claus plant emissions and increasing sulfur recovery are available.
4. Major energy users in the processes are oxygen production, acid gas removal, and gas compression.
5. Since essentially no tars or hydrocarbons are produced in entrained flow gasification processes, water cleanup problems are minimal and should cause no unique waste water treatment problems for conventional water treatment methodologies. Dissolved compounds such as  $NH_4$ ,  $H_2S$  and  $HCN$  and leached trace elements are the contaminants of concern. Waste water will be cleaned and recycled for process use. Chronic loss of water results from direct contact cooling tower operation. Control of losses from evaporative cooling towers is a major concern.
6. Large quantities of ash and slag will be generated with commercial gasification processes. An assessment of ash compositions and ash disposal techniques should be undertaken to determine the adequacy of current control methodologies.
7. Although much information has been written about coal gasification processes, there are many areas in which data is lacking in the environmental aspects of the processes. These areas include: 1) determination of the fate of trace metals, especially those considered to be volatile and hazardous, 2) quantification of volatile emissions from cooling towers,

slag prices, 5) determination of volatile substances ( $H_2S$ ,  $NH_3$ , and organics) from clarifiers and slag quench tanks, 6) determination of the chemical properties of clarifier effluent and sludge, and 7) a better general characterization of most process streams.

## RECOMMENDATIONS

This study and previous studies reveal that, with the possible exception of trace elements, adequate control technology is commercially available. Improvements in these technologies are needed to reduce energy requirements and environmental releases. The major need is to demonstrate that the control systems give adequate cleanup with actual process streams. This can be done in two ways:

1. Characterize flows and control equipment performance in existing operating plants.
2. Install production capacity based on the gasification technologies and thoroughly characterize flows and environmental releases at these installations.

The first option involves getting permission from operating plants to instrument their facility to determine process flows and to monitor the area surrounding the plant. EPRI funded a study on gasification of COED char in a K-T gasifier at Puentes, Spain. The report on the results of this study has not been issued at this time. The fact that COED char was gasified in a K-T unit at Puentes, Spain, indicates that cooperation with operating plants and foreign countries is possible. However, operators are usually very sensitive concerning studies relating to environmental releases, and the flexibility in modifying or changing processing conditions would be severely limited in testing at a commercial facility.

Installation of production capacity based on these gasification technologies is the recommended approach. Rather than install units in a highly industrialized area such as Cedar Bayou, Texas, as recently announced,<sup>25</sup> it is recommended that units be installed where effects of trace elements and other releases can be thoroughly characterized.

The following steps are recommended to demonstrate the adequacy of environmental control technology for gasification:

- Install a 300 t/d (or larger) ammonia fertilizer plant in a non-industrialized area.
- Thoroughly characterize the state of the environment at the plant location before operations begin.
- Monitor releases from the plant during operations. Determine all process flows in the operating plant.
- Determine trace element behavior to see if any mechanisms for accumulation of toxic quantities are acting.

Successful demonstration of the project in an industrially undeveloped area would answer questions of environmental concern. Results would be extremely valuable in establishing environmental standards. This would allow employment of a technology to use coal to produce a product that is presently a large consumer of dwindling supplies of natural gas.

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Coal conversion processes employing wet cleaning of gases transfer a major fraction of coal chlorides and fluorides to the gas condensate. The presence of halides and other strong electrolytes, absorbed from the gas or leached from particulates, compromises the prospects for reuse of the condensate.

Preliminary absorption of halides involves a controlled two stage quench that collects particulates and absorbs strong electrolytes in a segregated, low volume, primary condensate. The larger volume secondary condensate collected from the second stage quench is amenable to partial desalination by steam stripping of volatile weak electrolytes and biological treatment for removal of organic compounds.

A study was made to assess the technical and economic feasibility of two stage gas quenching at a hypothetical producer gas plant operating on alternate feeds of high halide Eastern coal and low halide Western coal. The results indicated that a first stage quench collecting 10 percent of the total condensate would absorb over 99 percent of gas chlorides and over 97 percent of gas fluorides. Some thiocyanate was presumed to collect in the secondary condensate that compromised the efficiency of weak electrolyte removal by steam stripping and biotreatment. The ratio of electrolyte concentration for treated primary condensate to treated secondary condensate for Eastern and Western coals was 89 to 1 and 18 to 1 respectively. Comparative cost estimates of two-stage quenching versus single stage quenching with desalination of effluent by reverse osmosis indicated that two-stage quenching was more economical for high halide Eastern coal and that reverse osmosis was more economical for low halide Western coal.

It was concluded that the two stage quench system was economically favored as compared to reverse osmosis desalination of single stage condensate where the gasifier gas contains high halide content and/or high moisture content. The two-stage concept is considered to be widely applicable to coal conversion processes employing wet gas cleaning.

The mechanism and location of thiocyanate formation in two-stage quenching was not defined in the study. If thiocyanate forms during the first stage quench it is purged with the high electrolyte discharge. If thiocyanate forms during the second stage quench it will add to the electrolyte content of the secondary condensate that is reused in the process. Research is indicated to resolve the thiocyanate question as well as to any special materials requirements for the first stage quench system.

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Coal conversion processes employing wet cleaning of gases transfer a major fraction of coal chlorides and fluorides to the wastewater discharge. The presence of halides and other strong electrolytes in wastewater compromises the prospects for reuse, unless resort is made to energy intensive desalination technology.

An alternate concept to desalination involves the application of a two-stage gas quench where the first stage preferentially absorbs strong electrolytes in a low volume flow and the second stage comprising most of the condensate is collected relatively free of strong electrolytes. Thus the preliminary absorption of halides and other strong electrolytes in a low-volume first stage quench produces a condensate from the second stage quench that is relatively free of strong electrolytes. The volatile weak electrolytes present in secondary condensates can be stripped from the water and the organic substances can be removed by bio-oxidation to yield an effluent that has a low dissolved solids content.

The purpose of the present study was the evaluation of the theoretical performance and economic feasibility of the two-stage gas quenching concept for a fixed bed coal gasification facility using 1500 tons per day of coal. The study compares the relative cost of two-stage quenching with single stage quenching plus equivalent desalination. The study examined both air blown and oxygen blown gasification technology, with air blown results selected for presentation herein. The analysis of performance is considered to be representative of tar producing coal gasification technology employing wet cleaning of producer gas. The analysis of practicality applies only to the system studied.

## PROCESS DESCRIPTION

The hypothetical gasification plant selected for the study employed five 300 ton per day fixed bed gasifiers for an operational capacity of 1500 tons per day of coal. The gasifiers were modeled after the pressurized, stirred, fixed-bed gasifier of the Morgantown Energy Technology Center(1). The gasifiers had an assumed diameter of 13 feet and were operated air blown at a pressure of 103 psia. Steam at a pressure of 110 psig and a temperature of 350° F was injected into the gasifier and the outlet gas temperature was estimated as 1050° F. The gasifiers were operated on Illinois No. 6 coal and Montana Rosebud coal with analyses as reported in Table 1. The Illinois No. 6 coal was selected as representative of a high halide Eastern coal. The Montana Rosebud coal was selected as representative of a low halide Western coal.

The gas from the hypothetical gasifiers was passed through a dry cyclone and a heat recovery system to yield a feed to alternative gas cleaning systems at a temperature of 400° F and a pressure of 95 psia. The first system illustrated in Figure 1 provided conventional single stage gas cleaning consisting of a venturi scrubber, a spray cooler and an electrostatic precipitator to produce a cooled gas at 110°F. The second system illustrated in Figure 2 provided two-stage gas cleaning consisting of a venturi scrubber followed by a sieve tray absorber in the first stage and a spray cooler

	<u>Ill. No. 6</u> <u>Coal</u>	<u>Montana</u> <u>Rosebud</u> <u>Coal</u>
	<u>wt%</u>	<u>wt%</u>
C	65.70	50.56
H	4.80	3.18
S	3.70	1.09
N	1.10	0.90
O	8.04	9.81
Cl	0.25	0.03
F	120ppmw	30ppmw
Ash	11.20	9.73
H <sub>2</sub> O	<u>5.20</u>	<u>24.70</u>
	100.00	100.00
Higher Heating Value, Btu/lb	11,750	8,611

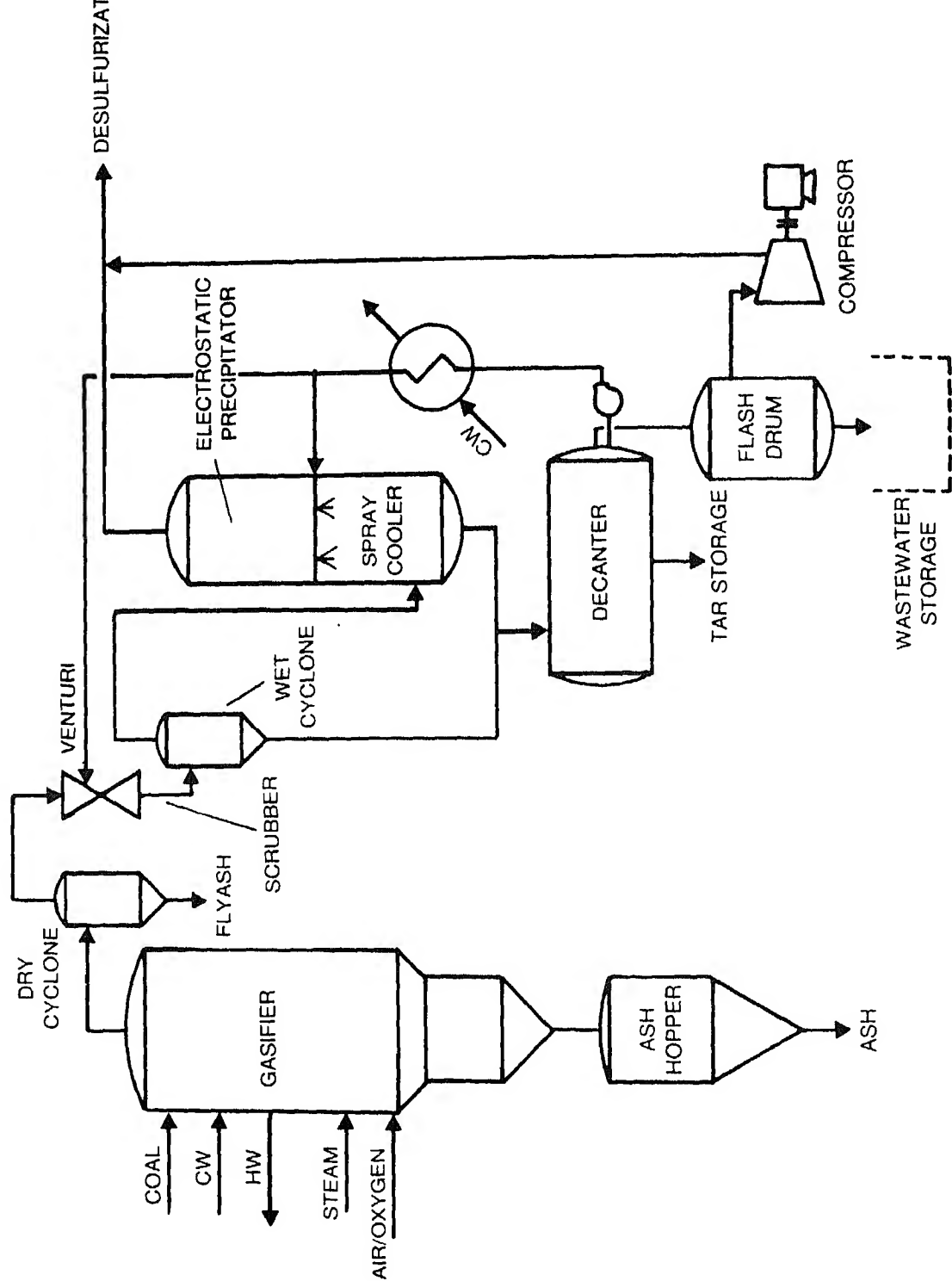


FIGURE 1: ILLUSTRATION OF PRODUCER GAS CLEANING BY SINGLE STAGE QUENCH

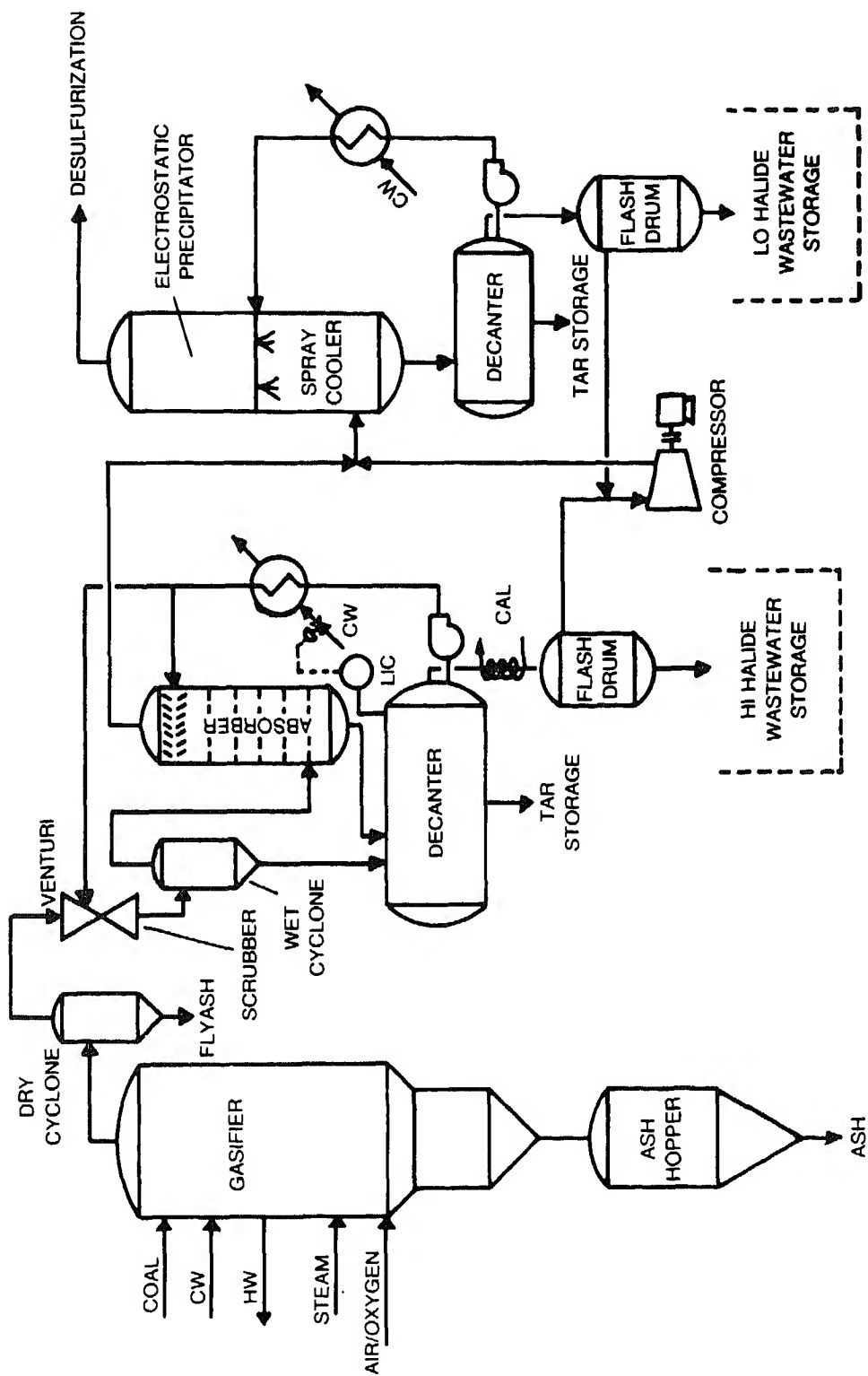


FIGURE 2: ILLUSTRATION OF GAS CLEANING BY TWO STAGE QUENCH

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condensation was controlled by operation of the first stage decanter on a variable level basis in conjunction with a controlled blowdown from the system. The selected blowdown rate was proportioned to the air feed rate to the gasifier. The temperature of the quench liquid was controlled by the level in the decanter so as to condense more water as the level in the decanter dropped.

Concepts for treatment of condensates collected from single stage and two-stage quenching are illustrated in Figures 3 and 4. The condensates discharged from the gasification process were stripped with steam for removal of  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , which were returned to the gas prior to desulfurization. Separate strippers were required for first stage and for second stage condensates. Sodium hydroxide was added to strippers operating on single stage and first stage condensates to free fixed ammonia. The addition of sodium hydroxide was not required for the stripping of second stage condensates.

The bottoms from the strippers were biologically treated by the activated sludge process for removal of cyanides, thiocyanates, phenols and other organics. The effluent was filtered by granular media filtration for capture of fugitive suspended solids. Separate treatment facilities were required for condensates from first and second stage quenching.

## METHODS

The study involved the conceptual design of process units, estimates of process performance and estimates of costs. The gas composition from the coal feeds given in Table 1 were estimated from material and energy balances keyed to operational data obtained from the MERC pilot plant stirred, fixed bed gasifier with heat losses taken as 2 percent of the total heat input. Where supplemental information was required for the analysis, performance projections were keyed to operating data from the Lurgi fixed bed gasifier at Westfield Scotland (2).

The chemical characteristics of the condensates were estimated with the assumption that equilibrium conditions were achieved in the absorption tower and in the spray cooler for the overhead temperature and pressure of each device. That is, the condensate blowdown was assumed to be in equilibrium with the vapor leaving the towers. Chemical equilibria were estimated by methodology of Edwards et. al. (3) supplemented by empirical correlations based on operational performance of similar systems.

The computer program (WAVES) developed in the reference predicts vapor liquid equilibrium for the system  $\text{NH}_3 - \text{H}_2\text{S} - \text{HCN} - \text{SO}_2 - \text{H}_2\text{O}$ . The program was modified to predict vapor liquid equilibrium for the system  $\text{NH}_3 - \text{CO}_2 - \text{H}_2\text{S} - \text{HCN} - \text{HCl} - \text{HF} - \text{H}_2\text{O}$  and applied to the prediction of condensate characteristics. The condensate characteristics predicted by the program were adjusted to include absorption of phenol, the presence of tar and the formation of thiocyanate. Thiocyanate formation is a complex phenomenon that was not resolved in the study. Based on coke plant correlations it was assumed that approximately 70 percent of the cyanide absorbed was converted to thiocyanate in the usual case where excess sulfur was present in the system.



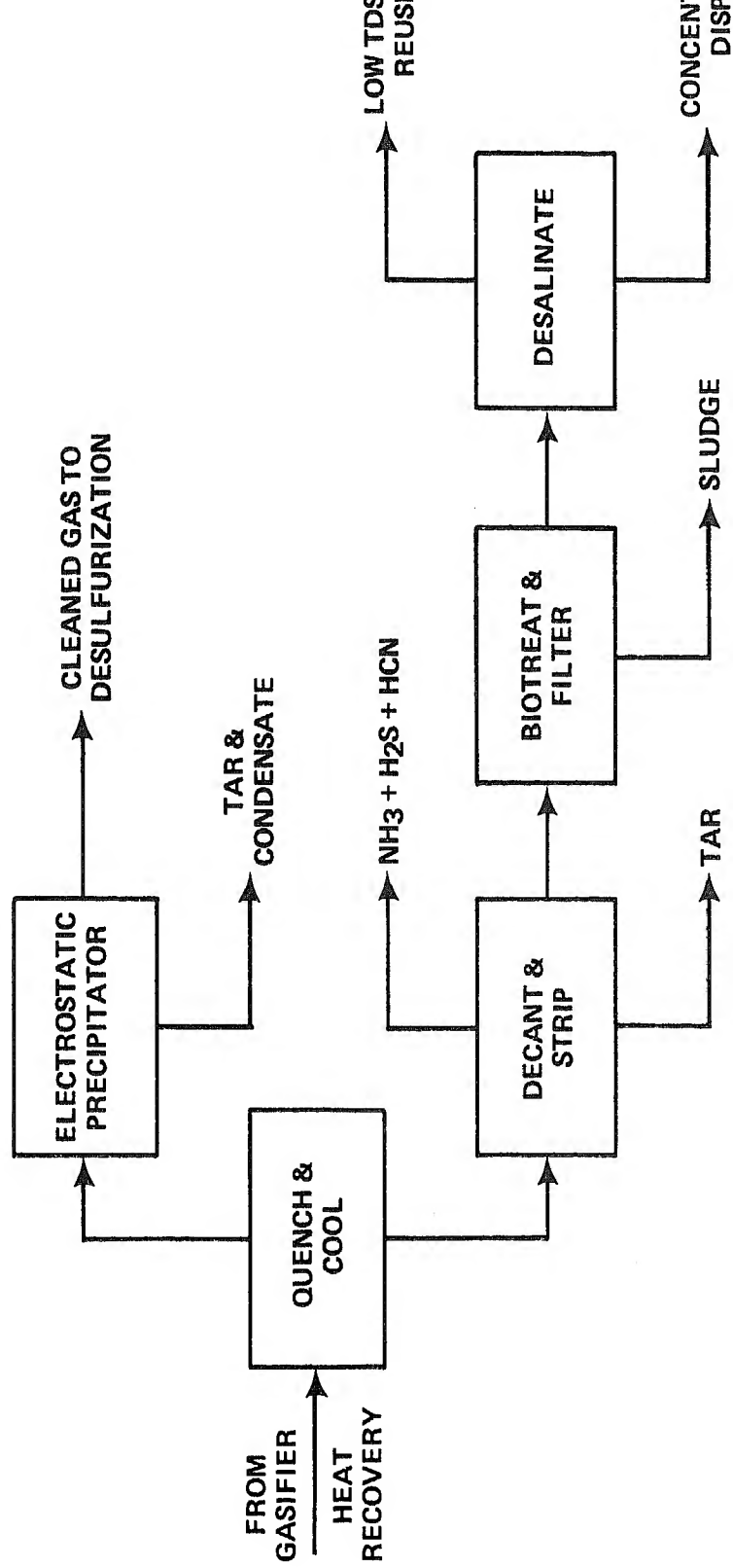


FIGURE 3: CONVENTIONAL GAS CLEANING AND CONDENSATE TREATMENT

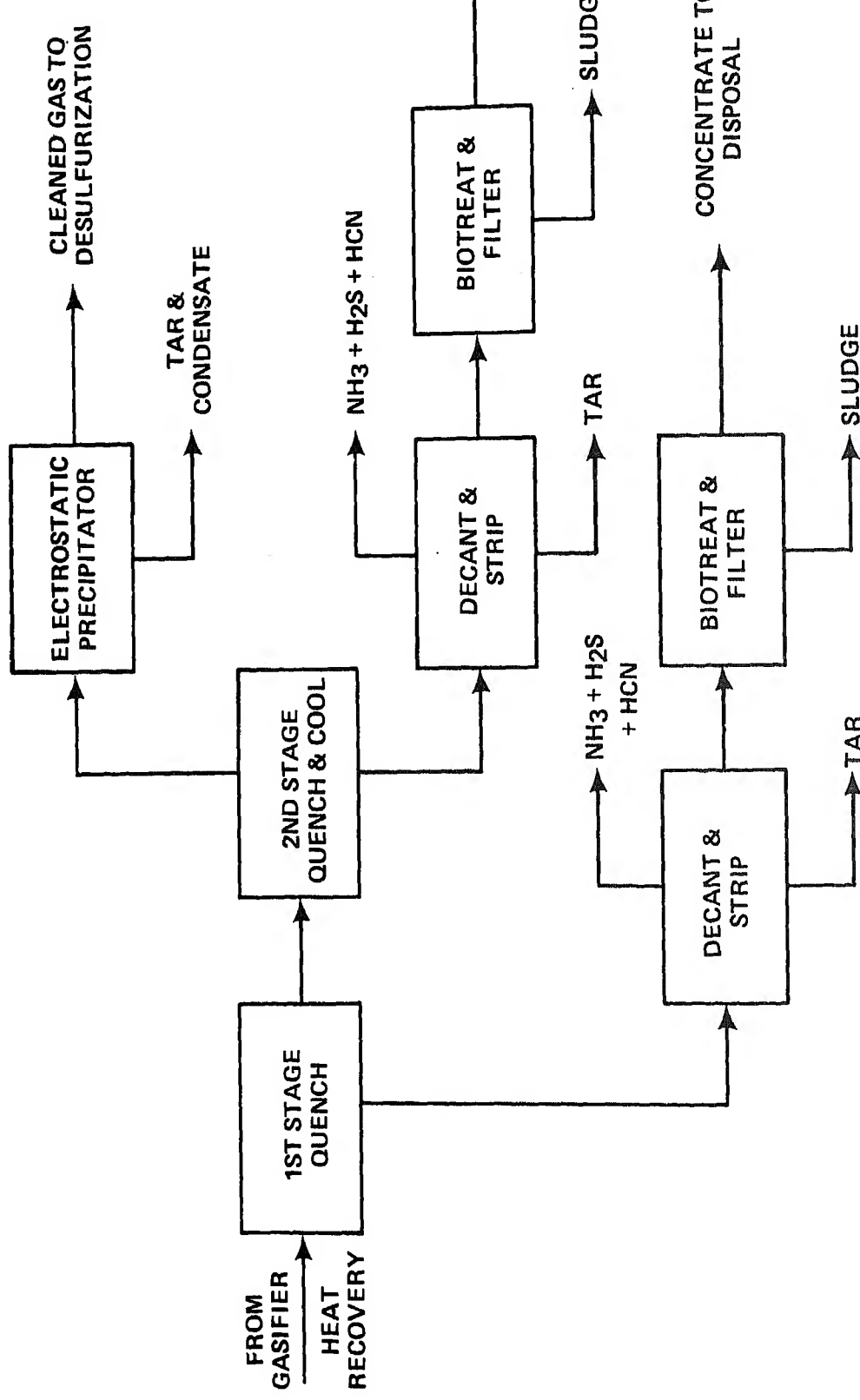


FIGURE 4: TWO STAGE GAS CLEANING AND CONDENSATE TREATMENT

residuals in the stripper bottoms of 50 mg/l of  $\text{NH}_3$  and 5 mg/l of  $\text{H}_2\text{S}$ . Estimates of residual concentrations in the stripper bottoms were based on analysis of vapor-liquid equilibria adjusted by performance correlations from coke byproduct plants and petroleum refineries (4)(5). Based on performance correlations, the phenol residual in the stripper bottoms was estimated as 80 percent and total cyanide residual was estimated as 60 percent of input values.

The activated sludge facilities consisted of equalization, aeration, settling, granular media effluent filtration and attendant sludge dewatering systems. The systems were designed to operate in a temperature range of from 75 to 95° F at a sludge loading of 0.05 lbs. phenol per lb. mixed liquor volatile suspended solids. The performance of the systems was estimated from correlations with waste treatment results at coke plants and gasification plants.

Order of magnitude estimates were prepared to enable comparison of costs of conventional single stage quenching with costs of two-stage quenching. The estimates were prepared from engineering flow sketches and sized equipment lists. The scope of the estimates encompassed the gas cleaning trains, wastewater storage facilities, wastewater stripper facilities and wastewater treatment facilities. Order of magnitude estimates were also prepared for wastewater desalination by reverse osmosis.

## RESULTS

The higher halide and sulfur contents of the selected Illinois No. 6 coal described in Table 1 as compared to the selected Montana Rosebud coal yielded higher concentrations of HCl and HF in the gasifier raw gas as indicated in Table 2. Residual concentrations of HCl and HF in the cooled gas leaving the gas train were less than 0.0001 percent of gasifier gas concentrations. Thus halides were projected to be substantially removed by effective wet gas cleaning. For a given coal, the cooled gas leaving the electrostatic precipitator had essentially the same composition whether processed by single stage or two-stage quenching.

Figure 5 illustrates the predicted relationship for HCl absorption as a function of the water condensed in the first stage quench. The combination of the venturi scrubber (15 in wg. pressure drop) plus the sieve tray absorber with 9 trays was indicated to remove 99.9999 percent of the chlorides from Illinois No. 6 producer gas at a condensation level of 20 gallons per ton of coal fed. This constituted essentially complete removal of chlorides in the first 20 gallons (7 percent) of a total of 290 gallons of condensate produced per ton of coal fed. Somewhat higher absorption of HCl was projected for operation with Montana Rosebud due to increased alkalinity of the condensate.

The predicted removal of HF as a function of volume of condensate is presented as Figure 6. With producer gas from Illinois No. 6 it was projected that a first stage quench of 30 gallons per ton would absorb over 98 percent of the HF from the gas. This amounted to 98 percent removal of fluoride in the first 10 percent of the total condensate. Fluoride removal from gas produced from Montana Rosebud was predicted to be higher because of increased alkalinity in the condensate. Thus the concept of preliminary absorption of halides was theoretically viable.

The projected results of steam stripping and biotreatment of condensates

	<u>Illinois No. 6 Mole %</u>	<u>Montana Rosebud Mole %</u>
CO <sub>2</sub>	9.56	11.72
CO	9.90	11.88
H <sub>2</sub>	15.01	16.32
H <sub>2</sub> O	30.73	21.23
CH <sub>4</sub>	1.59	1.69
C <sub>2</sub> H <sub>6</sub>	0.14	0.17
H <sub>2</sub> S + COS	0.47	0.22
N <sub>2</sub> + A	32.38	36.47
NH <sub>3</sub>	0.17	0.27
HCl	311ppmv	60ppmv
HF	28ppmv	11ppmv
HCN	<u>173ppmv</u>	<u>272ppmv</u>
	100.00	100.00
Higher Heating Value, Btu/scF	102.9	114.0
Gas outlet temperature °F	1050	1050
Operating Pressure Psia	103	103
Gas Flow SCFM	178,800	112,100

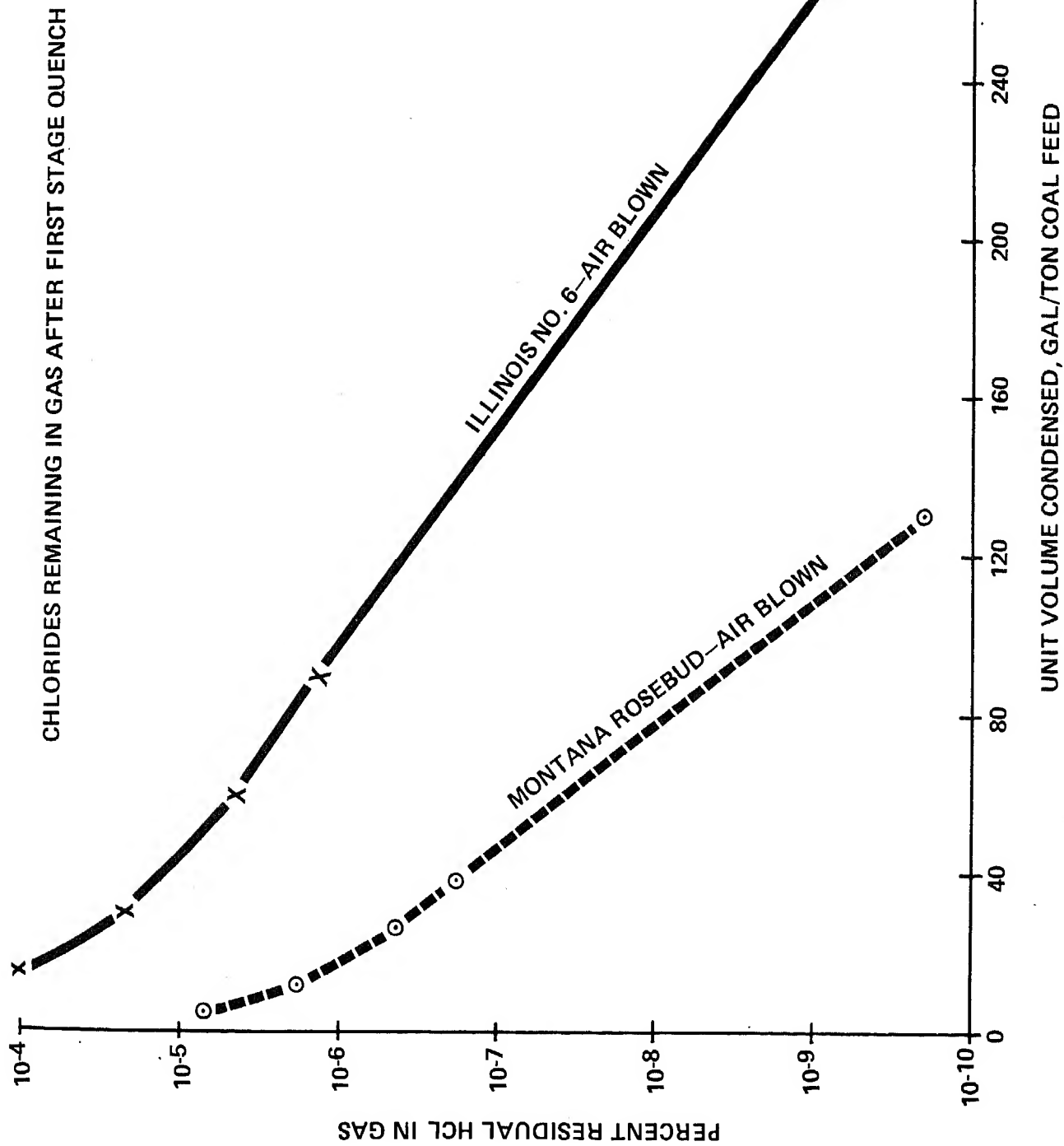


FIGURE 5: EFFECT OF UNIT VOLUME CONDENSED ON ABSORPTION OF CHLORIDES

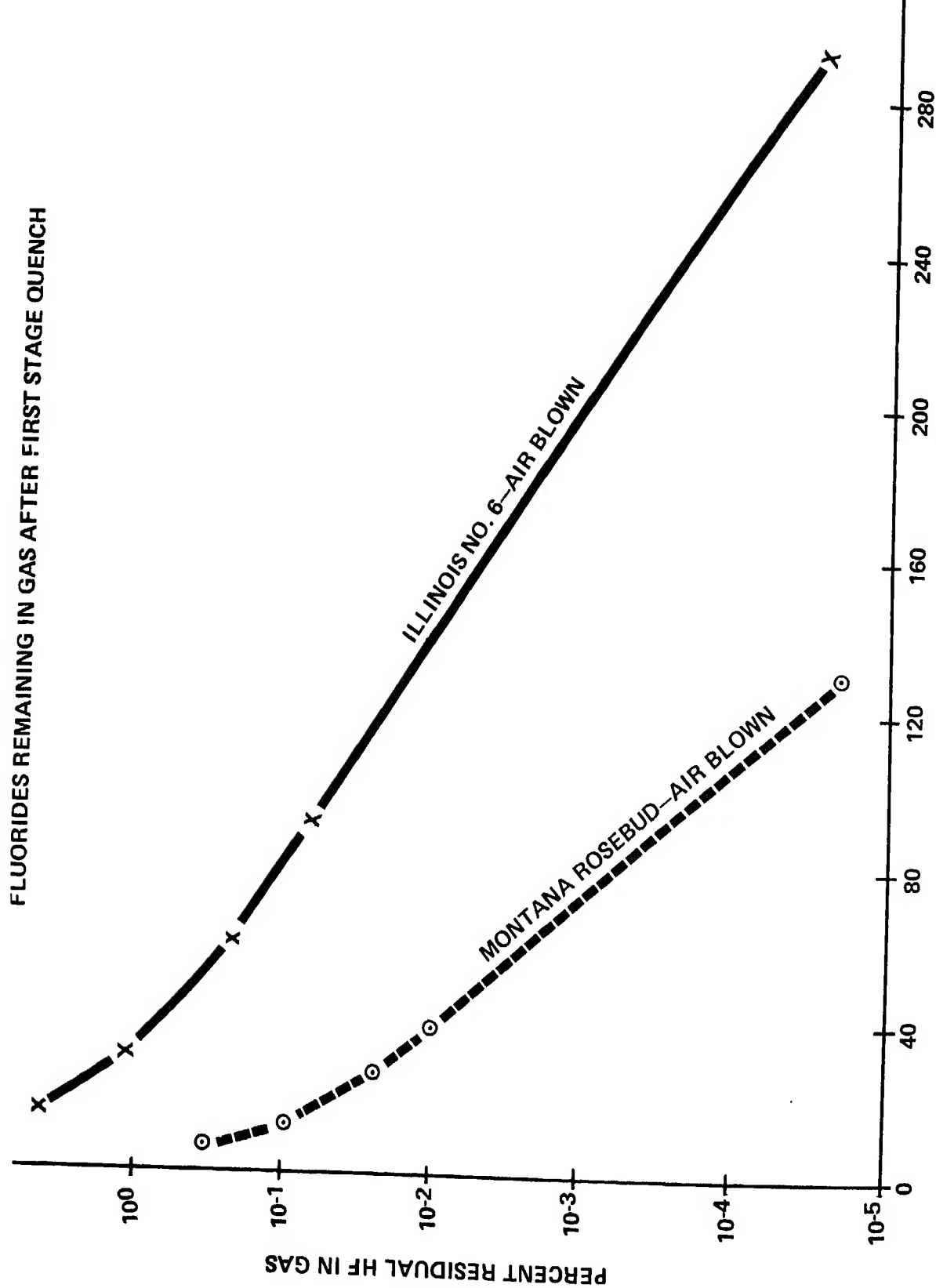


FIGURE 6: EFFECT OF UNIT VOLUME CONDENSED ON ABSORPTION OF FLUORIDES

Steam stripping was indicated to effectively remove volatile weak electrolytes such as  $\text{NH}_3$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . Free cyanide would also be quantitatively removed but it forms stable complexes of low volatility with metals such as iron and it reacts through various mechanisms with sulfur compounds during cooling of the gas to form thiocyanate - a strong electrolyte. Thiocyanate and metal cyanide complexes are refractory to the steam stripping process and therefore go with the stripper bottoms to biological treatment.

Biological treatment is projected to achieve excellent conversion of phenol plus substantial conversion of other organics and thiocyanates. The degradation of thiocyanate to ammonia and sulfate will contribute unwanted electrolyte to the second stage quench. The analysis projected that the strong electrolyte content of the second stage quench was 9 percent of a single quench and 1.1 percent of the first stage quench of 34 gallons per ton Illinois No. 6 coal feed. Thus the condensate from the second stage quench was of better quality for reuse than the condensate from the single quench.

The predicted results of steam stripping and biotreatment of condensates from gasifier operation on Montana Rosebud coal are presented in Table 4. The predictions forecast excellent removal of volatile weak electrolytes in the stripper and excellent removal of phenol by biological treatment. The strong electrolyte content of the second stage condensate was projected as 34 percent of the single quench condensate and 5.4 percent of the first stage condensate of 13.8 gallons per ton coal feed. The lower relative performance indicated for two-stage quench systems on Montana Rosebud was attributed to the lower halide content of the coal feed.

A cost comparison of single stage and two stage quench systems is facilitated by reference to Figures 3 and 4. The single stage quench will require a desalination operation to produce low electrolyte water for reuse whereas the two stage quench entailed the inclusion of a sieve tray absorber in the first stage quench and independent facilities for decanting, stripping and biotreatment of the first stage condensate.

Table 5 presents a comparison of estimated capital cost differences for the hypothetical gasifiers designed for airblown operation on Illinois No. 6 and Montana Rosebud coals. The capital cost for gas cleaning and condensate treatment systems was higher for two stage quenching than for single stage quenching. The difference was estimated as 2.2 million dollars for operation on Illinois Number 6 and 2.3 million dollars for operation on Montana Rosebud. The upgrading of single quench wastewater quality from Illinois No. 6 by application of reverse osmosis to attain comparability with the two stage quench was indicated to be cost ineffective. With Montana Rosebud the capital cost estimates indicated that there was potential for upgrading single quench water quality or for disposal to pond evaporation. Pond evaporation of single quench would feature a loss of the value of the second stage quench as makeup to reuse circuits. Pond evaporation was not evaluated for Illinois No. 6 operation inasmuch as it is not a viable alternative for the Eastern U.S.

A comparison of estimated annual costs is given in Table 6 for single stage and two stage quench systems with equalized reuse potential. Equalized reuse potential is taken as the separation of a reverse osmosis concentrate

Table 3: Effect of Treatment on Condensate Characteristics  
Illinois No. 6 - Air Blown

Component	Raw Condensate			Condensate After Stripping			Biotreated Condensate		
	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench
H <sub>2</sub> O gal/ton coal	292	30.1	262	293	33	261	294	34	259
NH <sub>3</sub> , mg/l	5310	10880	4671	50	52	50	44	24	42
CO <sub>2</sub> , mg/l	10740	360	11790	5	5	5			
H <sub>2</sub> S, mg/l	350	44	63	5	5	5	0.1	0.1	0.1
HCl, mg/l	2110	20480	<1	-	-	<1	-	-	-
HF, mg/l	104	1000	1.3	-	-	1.3	-	-	-
CN, mg/l	50	0.61	51	15	0.15	15	3.0	0.2	3.0
SCN, mg/l	260	3.2	275	171	1.9	177	10	2	10
Phenol, mg/l	3329	2209	3640	2640	1630	2920	0.1	0.1	0.1
pH	7.1	5.8	7.2	8-10	8-10	7-9	7.7	7.8	7.1
NaCl, mg/l	-	-	-	3460	29100	-	3380	29200	1
NaF, mg/l	-	-	-	230	1860	-	219	1870	2
SO <sub>4</sub> , mg/l	-	-	-		-	-	282	14	291
TSS, mg/l							25	25	25
Total Equivalent Strong Electrolyte, mg/l as NaCl							4028	31800	359
Concentration Ratio									
							11.3	89	1.0



Table 4: Effect of Treatment on Condensate Characteristics  
Montana Rosebud - Air Blown

Component	Raw Condensate			Condensate After Stripping			Biotreated Condensate		
	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench	Single Quench	10% Quench	Final Quench
H <sub>2</sub> O gal/ton	124	13.0	111	123	13.4	109	123	13.8	109
NH <sub>3</sub> , mg/l	11990	4866	12730	50	51	50	40	4	31
CO <sub>2</sub> , mg/l	27110	1888	29270	5	5	5	-	-	-
H <sub>2</sub> S, mg/l	199	75	225	5	5	5	0.1	0.1	0.1
HCl, mg/l	601	5718	>1	-	-	>1	-	-	-
HF, mg/l	60	574	>1	-	-	0.07	-	-	-
CN, mg/l	78	3.2	80	24	0.93	24	4.8	0.7	4.8
SCN, mg/l	410	16	-	270	11	279	10	2	10
Phenol, mg/l	6299	4675	7239	5056	3637	5824	0.1	0.1	0.1
pH	7.5	6.8	7.6	8-10	8-10	7-9	7.5	7.6	7.1
NaCl, mg/l	-	-	-	966	8619	-	976	8702	1
NaF, mg/l	-	-	-	127	1134	-	128	1145	1
SO <sub>4</sub> , mg/l	-	-	-	-	-	-	447	43	458
TSS, mg/l	-	-	-	-	-	-	25	25	25
Total Equivalent Strong Electrolyte, mg/l as NaCl							1649	10350	561
Concentration Ratio							2.94	18.4	1.0

Table 5

Estimated Capital Cost Differences for Single and Two Stage Quench Systems

	Illinois No. 6		Montana Rosebud	
	Single Quench MM\$	*Two Stage Quench MM\$	Single Quench MM\$	*Two Stage Quench MM\$
1. Gas Cleaning & Cooling	8.40	9.50	4.00	5.50
2. Condensate Stripping & Biotreatment	7.20	8.30	5.50	6.30
Sum of 1 & 2	15.60	17.80	9.50	11.80
3. Two Stage - Single Stage Difference with Effluent Equalized by:		+2.20		+2.30
4. Reverse Osmosis	+0.50			+0.70
5. Pond Evaporation	NA	NA	0	0

\*Condensate from first stage quench = 10% of input gas moisture

Table 6  
Estimated Annual Cost Differences for Single Stage  
and Two Stage Quench Systems with Equalized Reuse Potential

Cost Component	Illinois No. 6		Montana Rosebud	
	Single Quench \$/yr	*Two Stage Quench \$/yr	Single Quench \$/yr	*Two Stage Quench \$/yr
A. Quench & Condensate Treatment				
Operation @ 2.25 men		45,000		45,000
Maintenance @ 1.0% of Capital Cost		22,000		23,000
Misc'l. LS		5,000		5,000
Capital Recovery @ 20%				140,000
B. Reverse Osmosis				
Operation & Maintenance	330,000		110,000	
Capital Recovery @ 20%	100,000			
Subtotal	430,000	72,000	110,000	213,000
Excess Annual Cost	358,000			103,000

\*Ten percent of gas moisture condensed in first stage.

reverse osmosis operating on Illinois No. 6 coal is more expensive by about 360,000 dollars per year than a two stage quench system. The finding is considered characteristic of high halide coals.

With Montana Rosebud coal, the analysis in Table 7 suggests that the two stage quench system is more expensive by about 100,000 dollars per year than the single quench system plus reverse osmosis. The finding is considered characteristic of low halide coals that yield a small volume of condensate.

## DISCUSSION

The applicability of a gas cleaning system using a two stage quench to effect preliminary absorption of halides has been indicated to be technically feasible. The process objectives of capture of particulates, absorption of strong electrolyte gases and efficient demisting in the first stage quench were attainable by application of conventional process technology. The objective of control of the unit volume of first stage condensate was feasible by engineered application of a variable level first stage tar decanter. The analysis of benefits of the two stage quench are considered conservative inasmuch as the analysis was based primarily on absorption of HCl and HF. In actuality, the isolation of the secondary condensate from contact with flyash and volatilized salts would increase the contrast between the quality of primary and secondary condensates. The quality of the secondary condensate is expected to be far superior to the primary condensate. The combination of steam stripping and biotreatment of the condensate from the second stage quench is indicated to produce an effluent of low dissolved solids content. It is evident that the low dissolved solids effluent would be amenable to reuse as service water to the coal conversion process with substantially less upgrading than comparably treated condensate from a single stage gas cleaning process. Parenthetically it should be recognized that activated sludge effluents from treatment of coal conversion wastes characteristically contain low concentrations of organic matter - including some dark color bodies, so supplementary treatment would be required for some reuse applications.

The formation of thiocyanate during two-stage quenching is an enigma that was not resolved in the study. Appreciable thiocyanate is usually present in condensates from single stage quenching of producer gas and coke oven gas. It is established that thiocyanate can form as a result of reaction of free cyanide with sulfur, organic sulfur or oxidized inorganic sulfur (6) (7) (8). The dilemma in two-stage quenching is the estimation of the extent of thiocyanate formation in the second stage quench.

In two-stage quenching, the first stage quench cooled the gas to the 230-280° F range depending on the specific situation. It can be speculated that thiocyanate formation may occur in the first stage inasmuch as oxidized sulfur would be absorbed, and particulates bearing free sulfur and possible catalytic properties would be removed. Thiocyanate formed in the first stage quench would be removed from the process with the high electrolyte purge and would not register as electrolyte in the condensate from the second stage quench.

Thiocyanate formation in the second stage quench would be favored by the presence of organic sulfur, ammonia and cyanide as well as by temperature conditions. The limited availability of oxidized sulfur or external oxidant would presumably restrict reaction between cyanide and sulfide. However, reactions

is believed that the thiocyanate concentrations assumed to exist in condensates from the second stage quench were sufficient to cover the situation. It is conceivable that lower concentrations would be realized in practice -- which would register as improved quality of second stage condensate.

Absorption of HCl and HF in the first stage quench was assured by installation of a sieve tray absorber in conjunction with the venturi scrubber. The sieve tray absorber was the principal gas train component in the cost differential between single stage and two-stage quenching. It follows that cost savings would be realized if the combination of venturi scrubber plus efficient mist eliminators could be experimentally verified as adequate from the standpoint of absorption. Absorption of HF was indicated to control the design of the absorption system. Efficient mist elimination between first stage and second stage quenches is essential.

The cost estimates were prepared on the basis of carbon steel vessels and tanks in the gas train. The high electrolyte concentration of condensate from first stage quench, combined with suppressed pH, could necessitate the application of special corrosion resistant materials. Consultation with chemicals industry design engineers produced the recommendation of titanium clad vessels and tanks. Consultation with coke byproduct plant design engineers produced the recommendation of carbon steel with the expectation that the units would be tar coated. The position of the author is that the materials situation warrants experimental investigation including the possible application of neutralization in conjunction with corrosion inhibitors. A requirement for exotic materials would compromise the cost analysis presented herein.

The applicability of biological treatment to the wastewater was assumed inasmuch as coke and gas house liquors have been biologically treated for over 40-years. However, it is also recognized that problems have been experienced with biological treatment of some coal conversion process wastes, especially when the electrolyte concentration was high (9). For study purposes it was assumed that treatment problems could be resolved by process modifications to suit the specific situation. Some reservation is also expressed regarding the applicability of reverse osmosis to substrates containing a variety of non-specific organic compounds. The record of the process is spotty for such applications, but some latitude is available by process modification.

## CONCLUSIONS

The following conclusions were developed during the course of the study:

1. The concept of preliminary absorption of halides and other strong electrolytes in a low volume primary condensate was indicated to be technically feasible for the gasification system studied. The essential features of the first stage quench are particulate removal, strong acid gas absorption and mist elimination. The technology is considered to be widely applicable to coal conversion processes employing wet gas cleaning.
2. The two stage quench system was indicated to be economically favored as compared to reverse osmosis desalination of single stage condensate where the gasifier gas contains high halide content and/or high moisture content.
3. Thiocyanate in the secondary condensate was indicated as a possible limitation to water quality that was not quantified in the study.

The study results reported herein represent the accomplishments of many individuals on the staff of Arthur G. McKee and Company and elsewhere. Particular recognition is due: Dr. K. C. Vyas, Lead Alternate Fuels Engineer; K. J. Kosinski, Project Process Engineer; and E. S. Hayes, Project Estimator.

Valuable assistance was also contributed by Dr. G. D. Case and A. S. Moore, Jr. of the Morgantown Energy Technology Center and by Dr. Fred E. Witmer, Technical Project Officer, Division of Environmental Control Technology, DOE. The study was performed under Contract EE-77-C-02-4375 with the Division of Environmental Control Technology, Department of Energy.

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## 1. INTRODUCTION

Environmentally related studies of slagging fixed-bed gasification at the Grand Forks Energy Technology Center (GFETC) were initiated in 1976. A principal factor involved was the availability of a pilot-scale fixed-bed gasifier which could be quickly restored to operational status. Initially the pilot plant and gasifier was constructed and operated under the Bureau of Mines during the period 1958-1965 to demonstrate the feasibility of slagging operation and the parameters involved. The major objectives of the reactivated project are to develop: 1) a scaleable process data base on feed/product material balance, and 2) a detailed environmental assessment of the slagging fixed-bed gasifier (SFBG) process. The pilot plant has been operated in its original configuration for two years, however, plant and gasifier capabilities will be significantly expanded by modifications which are currently in progress. When modifications are completed and operation resumed, information will be obtained on a variety of test coals, including both low-rank non-caking coals (lignites and subbituminous) and bituminous coals with a range of caking characteristics.

The environmental assessment will include extensive sampling and analyses of process streams to characterize gaseous, solid, and liquid effluents, and testing of pilot plant-scale simulations for treatment of liquid effluents to establish the feasibility of zero discharge of liquids and safe disposal of solid wastes. The objectives of the GFETC project directly support the application of the slagging fixed-bed gasification technology to commercial development. The 25 ton/day gasifier has, at present, the unique capability of generating coal-specific data at reasonable cost for the large number of candidate U.S. coals.

In the particular area of liquid effluents and their treatment, a major part of the assessment performed on the SFBG is believed to be substantially applicable to fixed-bed, dry-ash gasifiers proposed to be used in first generation SNG plants. This will be validated, if possible, through comparative tests or bench-scale simulations. The GFETC gasifier can then provide information desired by the public on specific feed coals proposed for dry-ash SNG projects and industrial applications.

## 2. DESCRIPTION OF PILOT PLANT FACILITIES

The gasifier at the Grand Forks Energy Technology Center is a pilot-scale version of a conventional pressurized fixed-bed gasifier. In the commercial "dry-ash" process, gasification temperatures are maintained sufficiently low by the use of excess steam to allow removal of the ash in

to dry-ash removal operation. The steam consumption per unit of coal gasified in a slagging gasifier is about one-fourth of that required for a dry-ash unit, while at the same time, the gas production capacity per unit cross-sectional area is as much as three or four times that of the dry-ash gasifier.

Figure 1 is a cross-sectional view of the original GFETC gasifier. Coal is batch-charged to a lock hopper and gravity feeds into the main body of the gasifier. The coal is heated by the countercurrent flow of hot gases. As it descends, coal is first dried and then carbonized. At the hearth area, only a residual char composed of carbon and ash remains. The oxygen/steam mixture is admitted through four tuyeres just above the hearth, where the gasification and combustion reactions occur. Temperatures at the hearth are sufficiently high to maintain the ash in a liquid state, and the molten ash drains through a centrally located taphole into a water quench bath. A slag is produced which resembles coarse sand. It settles to the bottom of a water-filled lock hopper and is periodically removed.

The flow diagram of the pilot plant system is shown in figure 2. The hot gases pass up through the fuel bed, heat the coal, and carry the tar, light oil, water vapors, and the gas produced during carbonization to the gas offtake. The product gas stream is, therefore, a mixture of desired gas plus a variety of condensibles and other components. This stream enters a washer where a spray of the aqueous fraction of gas liquor which is recycled and cooled condenses water, light oil, tar vapors, and removes entrained dust particles. Accumulations in the spray washer are periodically discharged. The gas is then cooled, depressurized, and passed through a coke-filled scrubber for final cleanup before it is metered. Up to 1 ton/hr of lignite can be gasified in the unit at a 400 psig operating pressure.

The objectives and capabilities of the GFETC pilot plant program were expanded beginning in early 1977. Two major changes are involved. The pilot plant and gasifier are being modified to provide the capability to: 1) operate continuously for periods of 5 to 7 days, and 2) to test agglomerating coals. Design of additions or modifications to existing facilities of the Center was initiated, and construction phases are in progress. The gasifier will be relocated in an addition to the existing pilot plant in which a centralized control room and laboratories for effluent-related functions will be provided, and a conveyor system for unmanned coal charging of the gasifier is being installed.

Modifications to the gasifier include: installing a stirrer which operates in the top portion of the bed, and providing a double coal lock charging system with feeders. A cross-sectional view of the modified gasifier is shown in figure 3. Auxiliary additions include gas liquor separation, storage, and incineration, and a nitrogen supply purge system. A schematic of the modified pilot plant system is shown in figure 4. A conceptual drawing of the gasifier and facility is shown in figure 5.



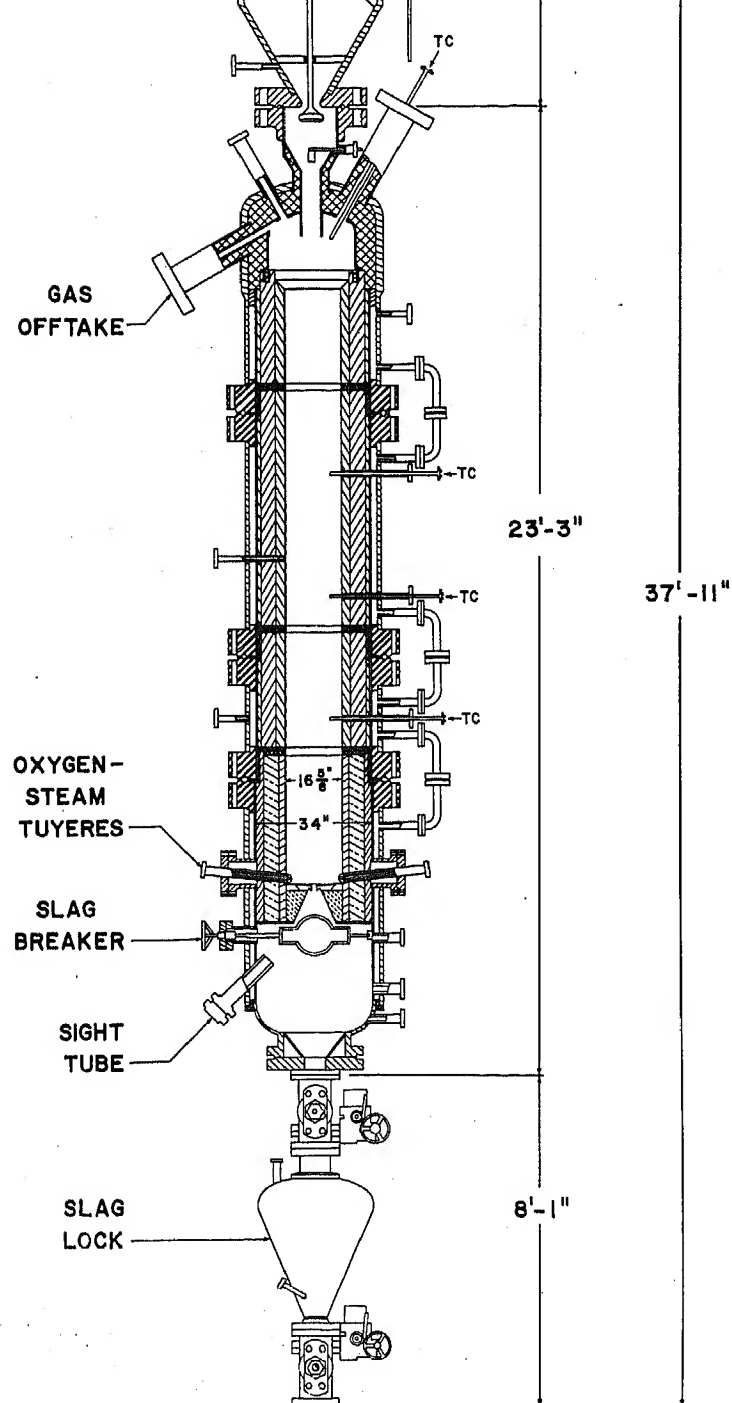


Figure 1. - Cross section of original GFETC slagging gasifier.  
Configuration used until September 1978.

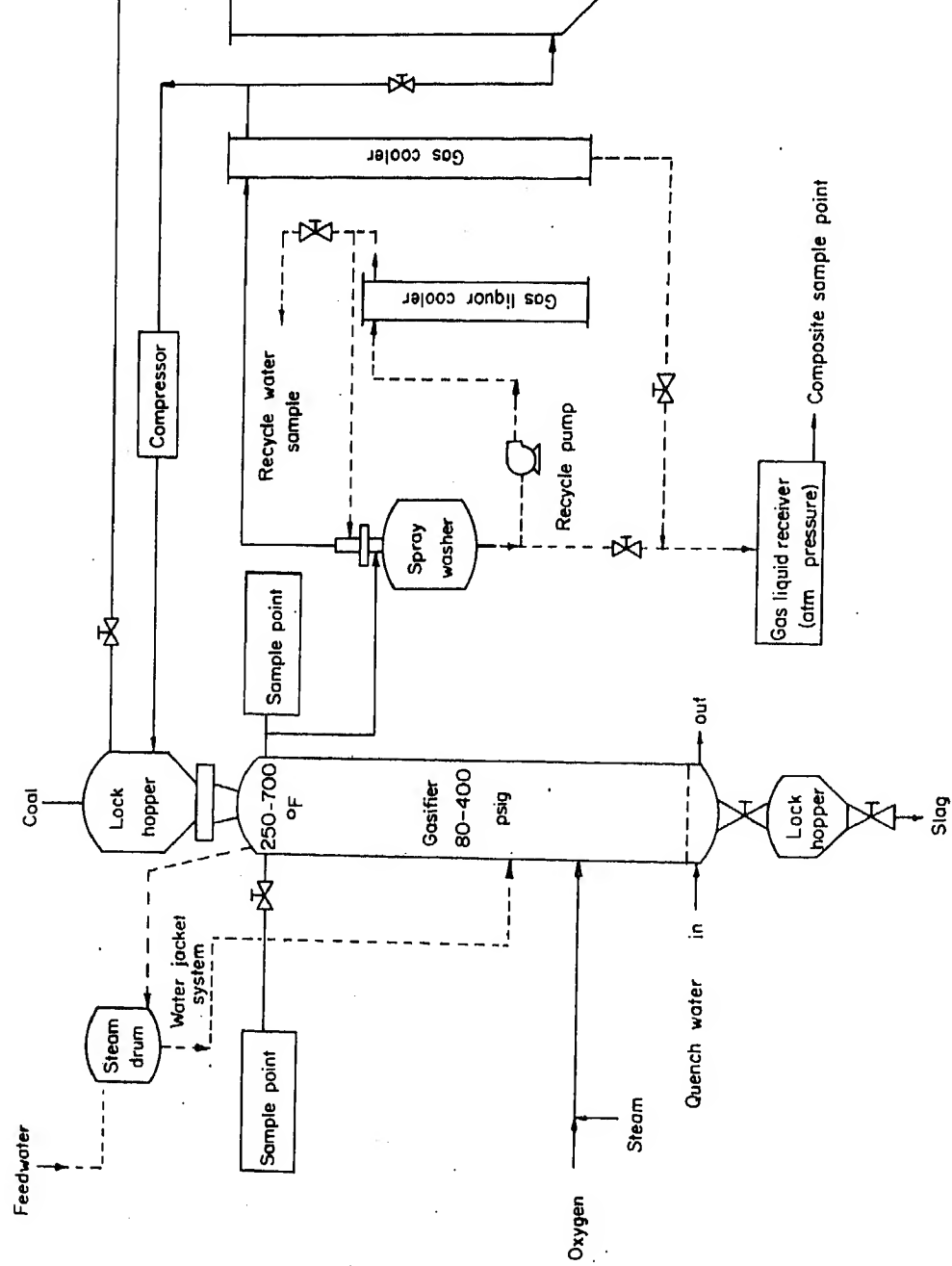


Figure 2. - Process flow diagram for the GFETC slagging gasification process

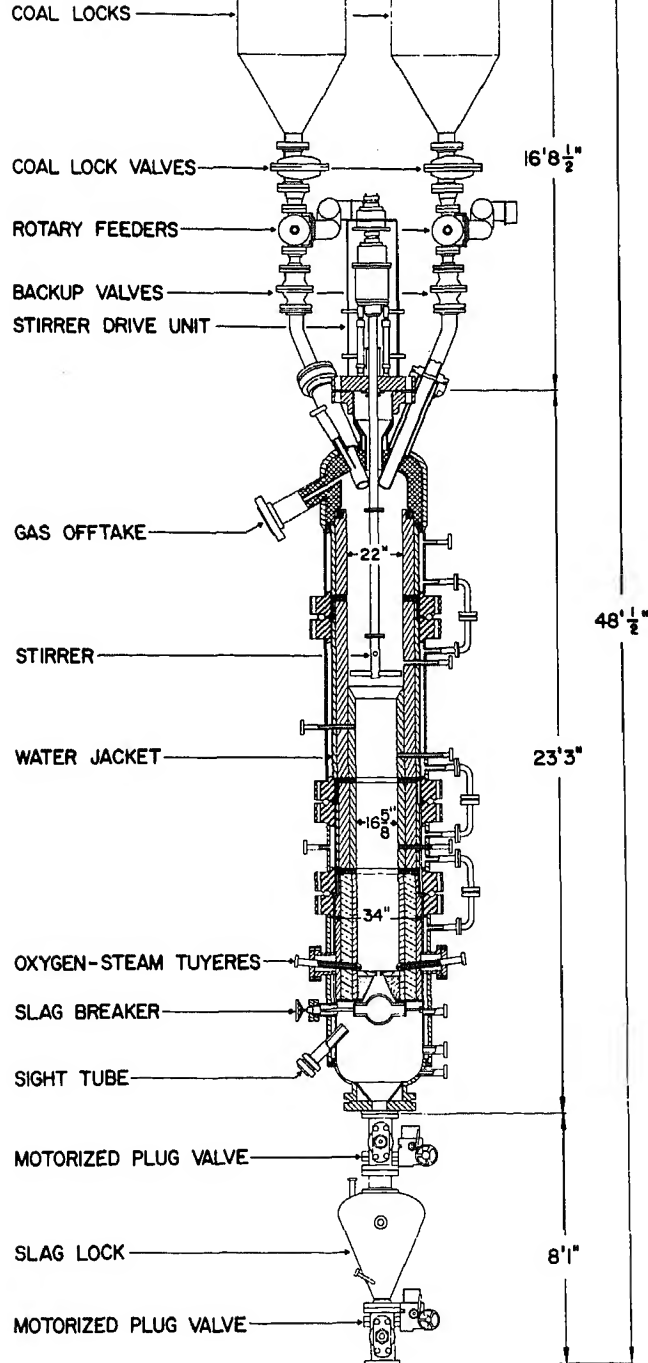


Figure 3. - Cross section of modified GFETC slagging gasifier.  
Operation planned for early 1979.

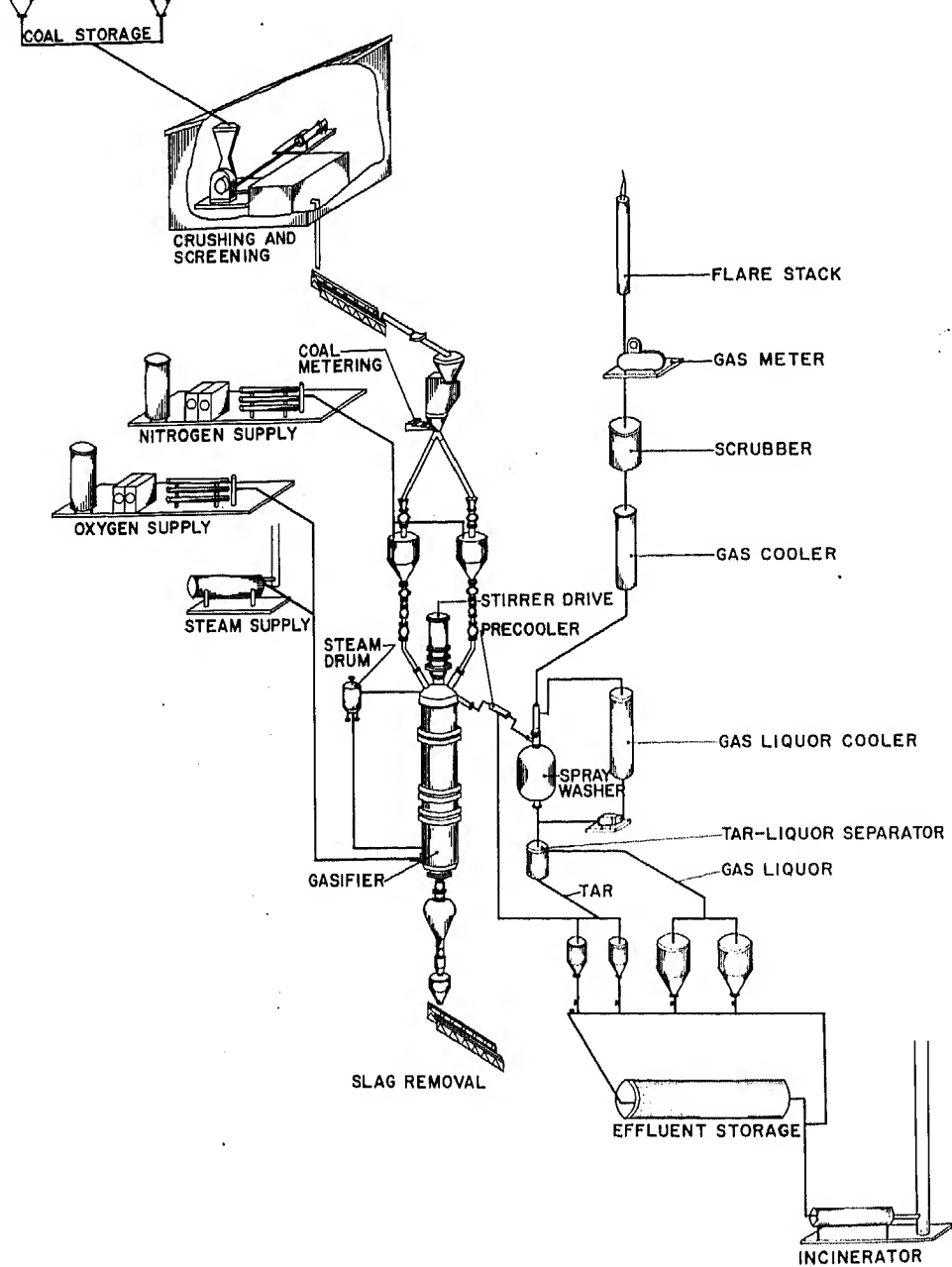


Figure 4. - Schematic of modified GFETC pilot plant.

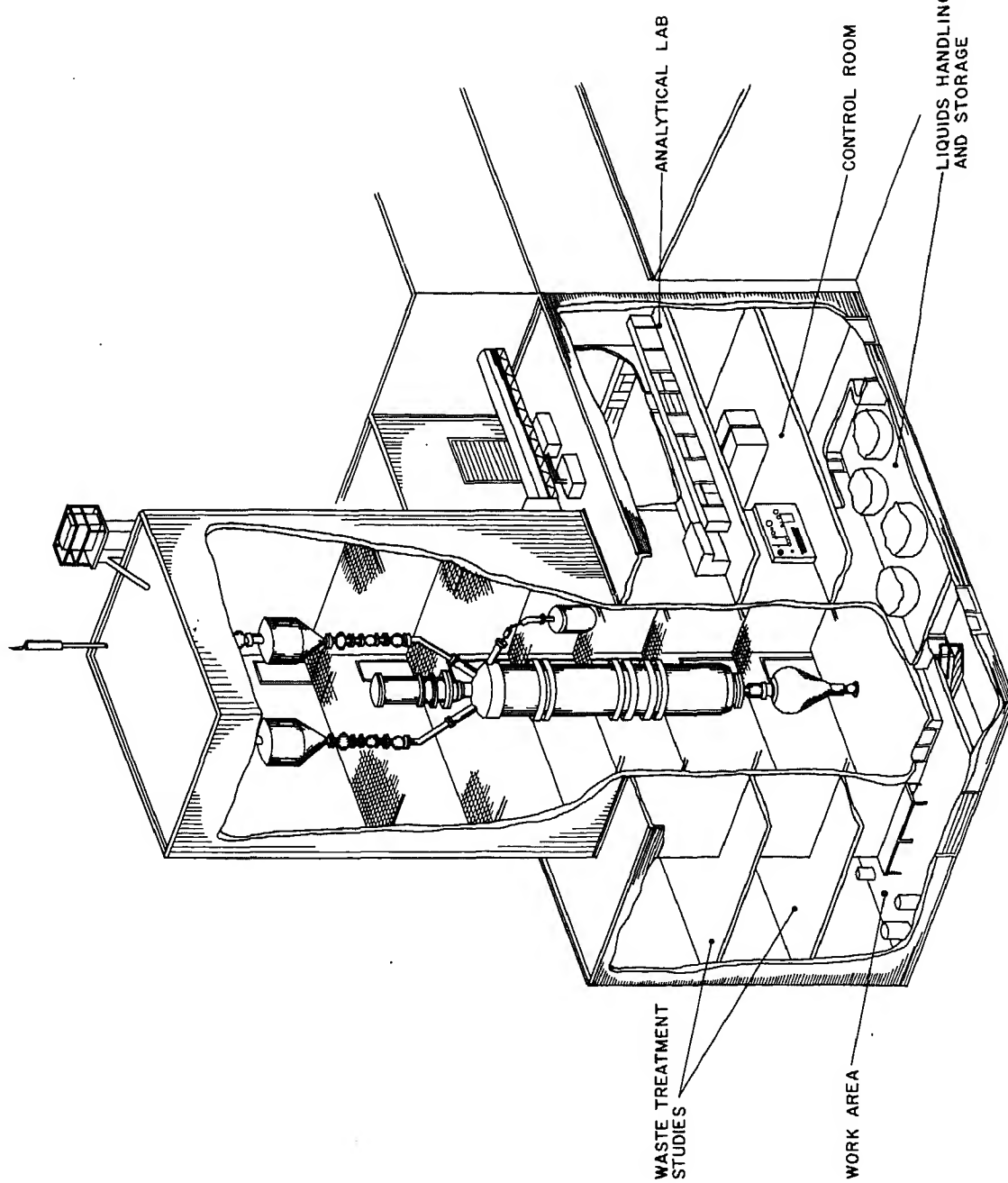


Figure 5. - Conceptual view of relocated SFBG and associated facilities.

for operation on bituminous coals, and the gas must be reduced prior to entering the spray washer. The precooler will also selectively remove tars and heavier components in the product gas when the lower moisture coals are used.

### 3. STRATEGIC APPROACH FOR ENVIRONMENTAL ASSESSMENT

The selective approach of the GFETC project is that the primary contribution which data from this oxygen-blown gasifier can make is to the direct application of SFBG technology in SNG plants. The information is expected to be used by future designers and operators, as well as state and federal agencies which are charged with licensing and regulating these plants. Data on specific coals will be made available to the public on gas contaminants, and process-produced tar, oil, and waste water. Since the principal unresolved and controversial problems attending operation of SNG plants are concerned with the treatment, use, and disposal of tar, oil, and waste water, studies will be performed to establish treatment techniques consistent with total reuse of water and zero discharge of liquids.

The gas liquors from the SFBG process are produced from the moisture in the raw coal and any process steam not reacted, the tar and oil originating from carbonization of the coal, plus a variety of organics and inorganics which are dissolved in the aqueous condensate. The process streams that result from treatment of gasifier effluents are device-specific -- that is, they depend on the particular hardware that is used. The treatment operations have, therefore, been designed to provide enough flexibility to ensure scaleable data, even in cases where specific hardware used may not be the type selected for future commercial application.

The treatment steps for the aqueous phase currently planned involve: 1) ammonia stripping, 2) phenol extraction, and 3) biological treatment. In addition, it is planned to study the suitability of waste water from various stages of treatment in a simulated cooling tower, the degree of oxidation or evaporation of residual organics, and the fouling of heat transfer surfaces. Studies relating to the tar-oil fraction include characterization and suitability for potential utilization schemes.

The product gas is extensively characterized and analyzed. Studies of gas treatment are underway elsewhere which address points of particular concern (e.g., studies on methanation at the Synthane Plant and at IGT), and the commercial technology is judged satisfactory with minimum refinement. For these reasons gas treatment is not being studied.

Solids produced in a commercial slagging gasification plant would include slag and a variety of sludges produced in water treatments. Slag from the pilot plant will be characterized in respect to analysis and leachability. Sludges, as they are produced in various pilot plant phases of the treatment studies, will be evaluated for potential disposal or utilization.

#### 4. SAMPLING AND ANALYTICAL METHODS FOR GASEOUS AND LIQUID EFFLUENTS

A major effort has been directed to developing and enlarging the capabilities for characterization of the gaseous and liquid effluents produced. In general, established techniques are verified and progressively modified to the process-specific conditions which exist.

Samples of offtake gas are collected regularly and routinely during operation and analyzed by gas chromatograph with a thermal conductivity detector. The instrument is calibrated with standard gases for: hydrogen, nitrogen, oxygen, carbon monoxide, carbon dioxide, hydrogen sulfide, ethene, ethane, propene, propane, iso-butane, and normal-butane. Approximately 20 additional hydrocarbons are indicated by GC analysis with a flame ionization detector. These components are being identified, and their determination will become routine. Sulfur gases, hydrogen sulfide, carbonyl sulfide, carbon disulfide, sulfur dioxide, and thiophenes, etc. are analyzed by separate GC with flame photometric detector. Methods are being developed for routine determination analysis of hydrogen cyanide, thiocyanate, and ammonia.

The major effluent stream of interest is the condensible fraction of the product gas -- the water and organics removed from the product gas stream in the gas quenching system. Obtaining representative and reliable scaleable samples has been a principal concern in present studies. Three different sampling methods are used. Method 1 consists of sampling the total quantity of liquids accumulated in the spray washer during each test. Degradation of certain chemical constituents due to system residence time, dilution effects due to the startup water in the spray washer, the effects due to high recycle rate of aqueous fraction, and the inability to collect samples representative of selected time periods are all problems of this method. Method 2 utilizes sampling systems which take a slip stream of the product gas at the gasifier offtake and pass it through a series of cyclones, condensers, and filters to remove the condensibles and particulates from a measured quantity of gas. Continued refinements have been made to solve the problems of sampling a dirty, high-pressure gas stream and to overcome inherent deficiencies associated with Method 1. The specific objective is to provide the capability to collect a reproducible, scaleable representative sample during selected short-time periods of operation.

Method 3 is a different approach to characterizing the production rate of the condensible effluents. It utilizes a gas chromatograph for on-line analyses. The technique being developed performs a simulated distillation of the coal tars produced with the product gas at intervals of 5 minutes. Identification of compounds by groups is being studied and appears to be feasible. This system is demonstrably capable of establishing rapid and short-term variations in tar-oil production rate, and possibly defining composition changes during short-term process upsets.

addition, organic compound identification by high-pressure liquid chromatography, pyrolysis GC/IR, NMR, and UV/Vis spectrophotometry is in progress and will greatly enhance the characterization efforts.

The aqueous phase of gas liquors normally contains ammonia, phenols, and acid gases. Ammonia and phenol are present at concentrations as high as several thousand mg/l. Routinely, the pH, alkalinity, phenol, o and m-p-cresol, ammonia, cyanide, sulfide and total sulfur, total organic carbon, and inorganic carbon content of aqueous phase is determined. Analytical development efforts are currently directed to the determination of trace organics present in the aqueous liquor fractions and as these techniques are established, will be added to the routine analytical base.

Determination of major, minor, and trace elements in effluents in order to establish material and elemental distribution in coal gasification is planned. Data will be reported for selected trace elements, including the following: antimony, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, gallium, germanium, lead, lithium, manganese, mercury, molybdenum, nickel, phosphorous, selenium, strontium, tellurium, tin, uranium, vanadium, zinc, and zirconium. Facilities of the Center include an ICAP analyzer for trace element determinations. At present, verification of procedures for sample preparation and processing are in progress and first efforts on selected samples have been initiated.

#### 5. RESULTS TO DATE ON CHARACTERIZATION OF GASEOUS AND LIQUID EFFLUENTS AND RELATIONSHIP TO OPERATING VARIABLES

Since May 1976, and until September 27 of this year, a total of 66 tests were scheduled with the Grand Forks pilot plant. Feedstock included three lignites and two subbituminous coals ranging in moisture content from 20 to 40 pct. Sustained operation was not achieved in the limited tests on subbituminous coals due to slagging problems or on one lignite of 40 pct moisture content due to the high moisture content. Samples and data in regard to effluent characterization were collected in 30 of the tests, principally on lignite from two mines, Indian Head (Mercer County, Central North Dakota) and Noonan (Burke County, Northwest North Dakota). Pressure was varied from 100 to 400 psi in 100-pound increments, and oxygen flow from 4000 to 6000 scfh, with corresponding steam inputs from 0.9 to 1.1 molar ratio of oxygen to steam.

Progressively, sampling techniques have been modified and refined, and efforts were directed to establishing test reproducibility, operational stability, and variability, particularly during upsets caused by coal charging. Samples from a variety of sampling locations and utilizing different techniques were systematically collected for comparison. Concurrently, analytical methods and techniques have been and continue to be progressively verified and modified as required.



utilized to produce quantity samples of aqueous liquor for biological treatment studies now underway at two facilities, and extensive effort was made to establish progressive changes in effluent characteristics as a function of operating time. Special effort was also made to determine change which occurred in effluent characteristics during the periodic upsets caused by coal charging and interruption of coal feed. These factors will be much less important in the modified gasifier when test periods of longer duration are possible, and the periodic upset during charging the single lock hopper will no longer occur. However, these data are required in establishing and assessing the validity of data collected in the program to date.

Since termination of operations at the end of September, efforts have been directed to compiling and evaluating the data. Typical fuel analyses for test lignites are given in Table 1. Moisture content of Noonan lignite "as tested" is not representative of the "as received" condition of 36 pct due to moisture loss which occurred in extended open storage, size preparation, and handling over the duration of the test operation. Data given in Table 2 illustrate the composition of gas produced. Both iso-butane and n-butane are now determined and found to be at the 0.01 to 0.02 pct range for gas produced from Indian Head lignite. Operating results at pressures ranging from 100 to 400 psig are given in Table 3. Effluent production of selected components in gas liquor as a function of operating pressure is given in Table 4. Effluent production and characteristics at identical operating conditions are compared for two lignites in Table 5. It is expected that when operations are resumed in the modified gasifier, tests will be conducted on test lots of the same lignites to compare results obtained with double lock feeding to those obtained with single lock operation.

A variety of publications and presentations have been prepared at the GFETC describing general and selected phases of the studies. These are listed as a source of additional information at the end of this paper.

## 6. PLANS FOR SEPARATION AND TREATMENT OF LIQUID EFFLUENTS

In the past, gas liquor that accumulated in the spray washer was periodically sampled and discharged to an external tank at atmospheric pressure. On completion of a run, all remaining liquor was drained to this tank. Tar, oil, and aqueous phases were decanted and drawn off separately, sampled, and analyzed. The composite end-of-run sample contained the liquor produced during the run and the startup city water required for initial operation.

The composite gas liquors contain an aqueous phase, a floating oil phase, possibly a sinking tar phase, and solid particles of dust, ash, and ungasified coal. Two improvements of the sampling and gas liquor collection system are being planned. The first involves continuous drawoff from the spray washer of two or three different phases--floating oils, heavy (sink) tars, and the principal aqueous phase. Secondly, a precooler will be installed between the gasifier and the spray washer with limited injection of

Proximate, pct:

Moisture.....	37.6	30.3
Volatile matter.....	25.7	28.2
Fixed carbon.....	30.5	35.4
Ash.....	6.2	6.1

Ultimate, pct:

Hydrogen.....	6.9	6.4
Carbon.....	40.9	45.9
Nitrogen.....	.5	.7
Oxygen.....	44.7	40.6
Sulfur.....	.8	.3
Ash.....	6.2	6.1

Heating value, Btu/lb.....	6780	7670
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Ash Fusion Temp., °F:

Initial deformation.....	2030	2070
Softening.....	2080	2100
Fluid.....	2130	2130

TABLE 2. - Typical product-gas analyses

Coal..... Run Number.....	Noonan RA-31	Indian Head RA-40
Gas Analysis, pct, N <sub>2</sub> free:		
CO.....	57.3	53.6
H <sub>2</sub> .....	30.5	32.5
CO <sub>2</sub> .....	6.4	8.4
CH <sub>4</sub> .....	5.1	4.9
C <sub>2</sub> H <sub>4</sub> .....	.2	.2
C <sub>2</sub> H <sub>6</sub> .....	.3	.3
C <sub>3</sub> H <sub>6</sub> .....	.09	.06
C <sub>3</sub> H <sub>8</sub> .....	.09	.04
H <sub>2</sub> S.....	.1	.2
COS.....	4.01	.01
Heating value, Btu/cu ft.....	340	333

Coal.....			Indian Head	
Moisture in Coal, pct.....	22.9	36.4	35.7	38.6
Test Conditions:				
Oxygen rate, std.cu.ft./hr. ..	4,000	4,000	4,000	4,000
Oxygen/steam molar ratio.....	1.0	1.0	1.0	1.0
Calculating period, hr. ....	7.15	6.08	11.92	8.68
<hr/>				
Fuel Rate (as-charged), lb./hr..	1,049	1,233	1,259	1,296
Fuel Rate (maf), lb./hr. ....	729	703	730	728
Product Gas Rate, std.cu.ft./hr. ....	20,108	20,759	21,994	21,039
Slag Rate, lb./hr. ....	72	55	67	50
Oxygen Consumption:				
cu.ft./1000 cu.ft. gas.....	198.9	192.7	181.9	190.1
cu.ft./1000 cu.ft. CO + H <sub>2</sub> ....	224.0	218.7	212.3	230.3
cu.ft./lb. maf fuel.....	5.49	5.69	5.48	5.49
Steam Consumption:				
lb./1000 cu.ft. gas.....	9.45	9.15	8.64	9.03
lb./1000 cu.ft. CO + H <sub>2</sub> .....	10.64	10.39	10.08	10.94
lb./lb. maf fuel.....	.26	.27	.26	.26
Production, cu.ft./lb. maf fuel:				
Gas.....	27.58	29.52	30.11	28.89
CO + H <sub>2</sub> .....	24.50	26.01	25.80	23.85
Product Gas Composition:				
CO <sub>2</sub> .....	5.0	6.6	8.4	10.5
Illuminants.....	.6	.3	.3	.2
H <sub>2</sub> .....	29.2	31.3	31.5	28.5
CO.....	59.7	57.0	54.2	54.4
C <sub>2</sub> H <sub>6</sub> .....	.2	.3	.3	.3
CH <sub>4</sub> .....	4.3	4.5	5.3	6.1

Run Number.....	RA-18	RA-36	RA-33	RA-38
Pressure, lb/sq in.....	100	125	200	400

1b/ton MAF Coal:

Tar.....	92	83	73	66
Water.....	1,044	1,404	1,408	1,378
Ammonia.....	7.8	9.1	9.6	12.7
TOC.....	10.0	11.4	12.3	12.9

water to condense tar, but without condensing the aqueous fraction. This precooler will be particularly important in operating on low-moisture (bituminous) coals where the offgas from the top of the gasifier may reach 900° F rather than the 320° F associated with lignite of 30 pct moisture.

The individual phases of the gas liquor must be separated for subsequent treatment. The aqueous phase of gas liquor, with tar and oil essentially removed, contains some suspended matter of colloidal tar/oil, dust, ash, and unburned coal. Ammonia and phenol can be removed by biological action, but past experience has shown that equipment size to provide required time generally precludes biological treatment of these substances at high concentrations. Both ammonia and phenol have market value, and proven commercial processes can successfully recover these from the gas liquor. Studies relating to development of improved techniques for their removal, therefore, have been given a low priority. Sour gas stripping and phenol extraction are being considered, however, as a means of producing representative waste water for biological treatment studies, both before and after phenol and ammonia removal. Although most investigations have been on aerobic digestion, anaerobic biological treatment offers some advantages and will also be considered.

Various physical/chemical processes, such as chemical and polymer coagulation and precipitation, multi-media filtration, activated carbon adsorption, ultra filtration, reverse osmosis, etc., are also candidate treatments to upgrade water qualities from gas liquor. Bench-scale experiments will be performed on selected methods to ascertain their applicability to the SFBG liquors, both as a primary treatment or as a polishing technique.

The major use of treated water at proposed gasification plants is in cooling towers. From an economic standpoint, the less treatment gas liquor requires prior to use in a cooling tower, the better. In any case, removal of tar, oil, and the major portion of the phenol and ammonia would be required prior to use of liquor in a cooling tower. A small pilot-scale cooling tower is being considered to operate on gas liquors as produced in

Run Number.....	RA-31	RA-40
Coal.....	Noonan	Indian Head
Moisture in Coal, pct. ....	30.3	34.7
Operating Pressure, lb./sq.in. ....	200	200

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Production, lb./ton maf:

Tar.....	90	70.2
Water.....	1,140	1,220
Ammonia.....	12.6	11.0
Total organic carbon.....	13.3	12.3

Concentration of Selected Constituents  
in Aqueous Phase:

pH.....	9.3	9.5
Alkalinity, ppm CaCO <sub>3</sub> .....	30,020	25,410
Ammonia, ppm.....	10,220	8,440
TOC, ppm.....	10,000	9,460
Phenol, ppm.....	5,689	4,260
o-cresol, ppm.....	1,000	836
m-p cresol, ppm.....	3,317	1,671

Concentration of Selected Components  
in Tar Phase, pct:

Phenols.....	18.2	15.4
Naphthols.....	3.9	5.6
Dihydroxybenzenes.....	1.4	0.0
Naphthalenes.....	9.3	9.0
Aromatic hydrocarbons with 3 to 5 rings.....	8.5	8.2
Saturated hydrocarbons.....	10.2	22.0
Non volatiles at 300° C and 0.1 torr..	2.4	3.6
Average mol. wt. of volatile compounds.....	152.2	156.9

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## 7. SOLID AND SLUDGE EFFLUENTS

In a commercial coal gasification plant the slag, or ash produced, is a formidable quantity of material. For example, a 25,000 ton/day lignite facility may produce 2,000 tons/day of slag/ash which must be disposed of. Except for possible use as an aggregate or as a fill for leveling purposes, the probable disposal method for the slag is in a landfill, and most likely it will be returned to the mines from which the coal came. Slag produced in SFBG is believed to be not leachable, but if process water is used for quenching, it may contain leachable components. As leaching to groundwater is not permitted by regulatory authorities, either an extensive sealing operation will be required or the slag, as produced, must be shown to be essentially non-leaching.

The disposal of residual dissolved and suspended inorganic and organic solids from the various waste water processing and treatment streams must also be managed to prevent contamination of surface or groundwater or the atmosphere. It has been suggested that sludges produced may be valuable as soil conditioners and low-grade fertilizers in mine spoil bank revegetation programs.

Blowdown from a cooling tower will be high in dissolved (and possibly suspended) solids which must be disposed of. Some materials in the blowdown may be inherently toxic, as are cadmium and mercury, or they may be merely aesthetically unpleasant, as is iron. Other elements, such as sodium, calcium, and magnesium, may contribute undesirable qualities for use in irrigation, domestic, or industrial water uses. Evaporation of cooling tower blowdown will probably be necessary, either in an evaporation pond or by direct means using waste heat.

The characterization of these solids and wastes will continue at GFETC. Expansion of SFBG studies will utilize, to a large extent, established and on-going programs to characterize the leachability of such wastes and to develop other necessary information.

## 8. CONTRIBUTION TO ASSESSMENT OF BIOMEDICAL EFFECTS

The gasification of coal produces some materials which have been shown to have toxic and mutagenic effects. Inevitably, small amounts are released to the atmosphere or are brought into contact with workers in a gasification plant. The Grand Forks slagging gasifier pilot plant is a reasonable model for worker exposure, and it provides data that, with proper interpretation, permit environmental emissions to be estimated. The biomedical concerns have generated a large scientific effort. Using a variety of procedures, skin tests, inhalation tests, and gross toxicology, by ingestion and tissue analysis with appropriate test animals, and bacterial mutagenicity, the

In addition, health records will be maintained on workers engaged in coal processing activities at the Grand Forks Energy Technology Center to assist in determining any possible long-term effects relating to occupational exposures.

## 9. CONCLUSION

The SFBG at GFETC provides the opportunity to assess the environmental effects of fixed-bed coal gasification. Utilizing manageable test lots of coal, representative effluents will be generated for verification of treatment and control processes or development of improved techniques. The capabilities and potential of the modified pilot plant will expand the operational and environmental data base available for commercial development of a viable SNG industry in the U.S.

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# OVERVIEW OF THE SYNTHANE PILOT PLANT ENVIRONMENTAL ASSURANCE PROGRAM

By

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## ABSTRACT

An historical account of the development and current studies of environmental monitoring and compliance at the SYNTHANE pilot plant will be presented. This account will include the experiences and problems in establishing monitoring programs in the following areas:

### Air:

- Ambient Monitoring
- Stack Testing
- Fugitive Emissions

### Noise:

- Background
- In Plant

### Water:

- Surface Water Control
- NPDES\* Sampling
- Continuous Water Monitoring

### Solid Waste:

- Characterization
- Disposal

### Occupation Health:

- Problem and Direction

In February and March 1975 the first ambient air background studies were undertaken at the SYNTHANE pilot plant. Subsequent to these initial studies an environmental monitoring and compliance program was developed incorporating the areas noted above. The cost of this program to date plus facilities and equipment amount to approximately three (3) million dollars. The experience provided in interfacing with the technology development and developing the environmental monitoring and compliance program can be of value to all who are involved in small scale and large scale development.

\*National Pollutant Discharge and Elimination System.

The Environment & Conservation Division of the Pittsburgh Energy Technology Center, Department of Energy, was formed on July 1, 1975. The charter under which this division operates in the environmental area focuses on the assessment of pollution potential from coal conversion processes and the evaluation of alternative techniques for reducing the environmental impacts of these technologies. This paper presents an overview of the comprehensive monitoring and assessment of the SYNTHANE pilot plant.

As of December 1, 1978, US DOE Headquarters terminated operations at the SYNTHANE pilot plant. Subsequently the majority of the programs discussed in this report have been or will shortly be discontinued. This report will attempt to highlight important considerations in designing and implementing an environmental monitoring program for other pilot plant operations.

The major assessment efforts can be appropriately divided into five areas in which most environmental legislation is also categorized--air, water, noise, solid waste and occupational health.

### Process Description

The 72 T/D SYNTHANE Coal Gasification pilot plant converts coal to high BTU synthetic pipeline gas. Basically there are five major steps in the process: (1) pretreatment, (2) gasification, (3) shift conversion, (4) purification, and (5) methanation.

Pretreatment: The coal is crushed to -20 mesh, dried with hot flue gas generated from the combustion of No. 2 fuel oil, then pressurized in lock hoppers with CO<sub>2</sub>. It is then pretreated at operating pressure with a steam-oxygen mixture. This mild oxidation destroys the caking properties of the eastern coals so that they do not agglomerate in the gasifier.

Gasification: In the free fall coal feed mode of operation the coal overflows the pretreater into the gasifier, about 20 feet above the normal bed level. The coal falls through the hot gases rising from the fluidized bed and is partially devolatilized. When utilizing the deep bed injection mode the coal is fed below the top of the fluidized bed. In either mode steam and oxygen enter the gasifier just below the fluidizing gas distributor. The gasification reaction occurs in the fluidized bed. Char containing ash and unreacted carbon is transferred to a separate bed in the lower part of the gasifier vessel where it is cooled before being discharged to lock hoppers.

dioxide, and impurities, is passed through a venturi scrubber and a scrubber tower to remove carry-over ash, char, and tars.

\*Shift Conversion and Purification: The concentration of hydrogen and carbon monoxide in the gas is then adjusted to a three-to-one ratio in the shift converter by the reaction of CO with steam to produce  $H_2 + CO_2$ . The acid gases are absorbed in a hot-potassium-carbonate tower (Benfield process); carbon dioxide is reduced to below 2% and sulfur is reduced to 40 parts per million. (Regeneration of the potassium-carbonate solution produces a gas rich in hydrogen sulfide which is converted to elemental sulfur by the Stretford process). The remaining traces of sulfur in the product gas are removed by passing the gas through activated charcoal.

\*Methanation: Two systems for methanation of product gas were planned for testing--hot gas recycle (HGR) and tube wall reactor (TWR).

## I. Ambient Air Monitoring

### A. Background Study

The ambient air monitoring program for the SYNTHANE pilot plant began with an initial background study of the air basin in which the plant was sited. This initial phase was performed in February and March 1976 and served to provide a background data base with which to compare ongoing monitoring data as the pilot plant began operation. The background study consisted of the following data collection activities. The results of these data comparisons are available through the EC Division.

Four Hi Vol samplers were operated for a 24-hour period every six days. The locations are shown in Figure 1. The Hi Vol filters were weighed and analyzed for the following constituents: fine particulates, sulfates, nitrates, mercury, arsenic, nickel, lead, beryllium and cadmium. The prevailing 24-hour surface wind from Allegheny County Airport, located approximately 3.5 miles from the air monitoring network, was computed for each test along with other meteorological dispersion parameters. The data were then compared with all federal and state ambient air standards and analyzed to determine what the plant contribution was to the monitors.

\*The Shift Conversion and Methanation process steps were not operated throughout the life of the SYNTHANE pilot plant.

An eight-station sulfation plate network was operated utilizing fifteen-day exposure periods. The sulfation data was converted to PPM SO<sub>2</sub> by dividing the average sulfation rate of three plates located near the continuous SO<sub>2</sub> monitor at Site 1 into the average hourly SO<sub>2</sub> concentration for the fifteen-day period. This number was then converted to ug/m<sup>3</sup> SO<sub>2</sub> by multiplying it by 2620. The data were compared with annual ambient SO<sub>2</sub> standards and then analyzed to determine the plant contribution.

A dustfall network was utilized consisting of eight site locations. The dustfall jars were collected once a month and analyzed for total dustfall, water soluble particles and water particles. The results were compared with Pennsylvania State ambient standards.

In addition to the stationary sites a mobile van sampled the air basin. See Appendix A.

#### B. Six Month Air Quality Study

The second phase of the air monitoring program conducted August 1976 to January 1977 consisted of a six month study to assess the pollutant contribution of the pilot plant operation to the ambient air. These monitoring data were compared to the background data base to evaluate any change in the air basin. The method of data collection and parameter measurement for the six-month study was essentially the same as for the background study.

The pilot plant contributions to the Hi-Vol samplers were determined by plotting the prevailing 24-hour wind for each Hi-Vol unit on a map showing the location of each monitor and the SYNTHANE plant. A triangular area is drawn along the radial of the prevailing wind from the plant. The width of the triangle is a 15° arc on either side of the prevailing wind radial. (Note Figure 1.)

Monitoring parameters included CO, O<sub>3</sub>, NO<sub>x</sub>, SO<sub>2</sub>, Total Hydrocarbons (THC), H<sub>2</sub>S, Coefficient of Haze (COH), wind speed and direction, dew point and temperature. Under worst case assumptions, the concentrations at any monitoring site within this triangle measure the plant emissions. All other monitoring sites are considered to measure background. The difference between the average downwind concentrations and the average upwind concentration is considered to be the plant contribution. This of course is a worst case assumption which assumes that no other source exists between the plant and the receptor site. Extra care should be taken in interpreting the data with this assumption in mind.

# AIR QUALITY SAMPLING NETWORK

## HI-VOL DATA

### FINE

### PARTICULATES

SULFATES 4 SITE NO

NITRATES

RUN NO: 25

DATE: 12/24/76

GROUND INVERSION

STRENGTH 2.4 °C

TOP 1600 FT. MSL

DURATION

UPPER LEVEL INVERSION

STRENGTH

BASE

TOP

AFTERNOON VENTILATION

RATE 6400 M<sup>3</sup>/g

2-7-79 L-16496A

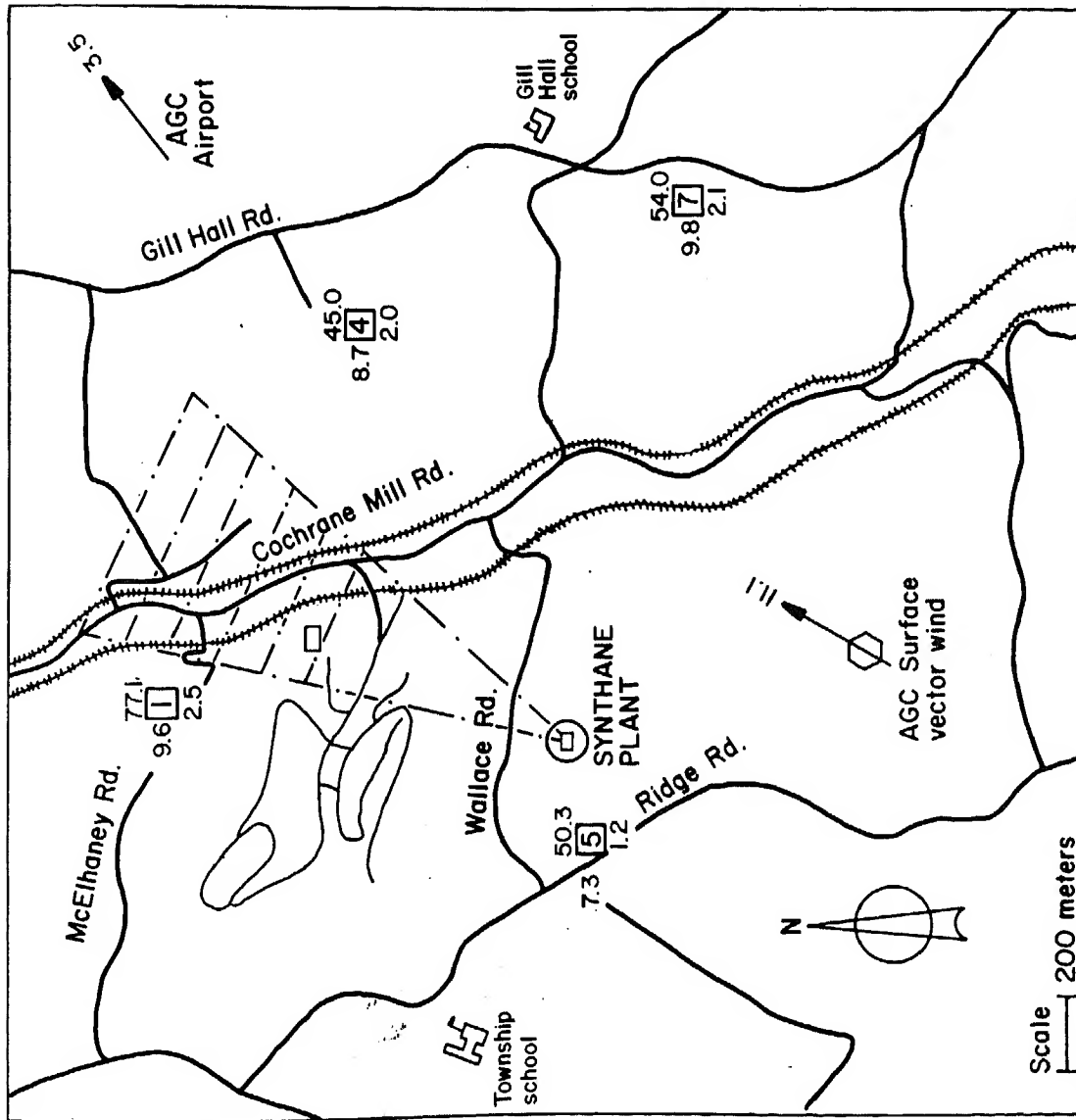


Figure 1 - Ambient air monitoring sites

### C. Continuous Monitoring Trailers

The background and six-month study provided a data base to evaluate the pilot plant contribution to the ambient air under certain operating conditions. However, the nature of pilot plant operations are such that changing conditions were anticipated to change emission characteristics. Some parameters affecting effluent characteristics include types of coal (high and low sulfur content), temperatures, pressures and fuel feed characteristics.

To properly evaluate these changing conditions, a continuous monitoring network was determined to be most cost effective as well as efficient. Two ambient air monitoring trailers were subsequently sited and put into operation in early 1977. Records containing SYNTHANE pilot plant operations data were maintained to compare with the data generated from the monitoring trailers. The correlation of these two information sources provided a means of evaluating changing process conditions relative to the ambient air.

The Hi-Vol samplers, dustfall jars and sulfation plates were retained from the background and six-month study as part of the continuous monitoring network. The only change in these data collection systems was analysis of the metals on the Hi-Vol filters. These were changed to provide a full survey for all metals potentially emitted from the pilot plant and to correlate them with the source testing.

The site source of the trailers were determined using the meteorological data base of the background and six-month study. The prevailing wind was delineated and one trailer was located upwind and one downwind of the plant. Physical interferences such as buildings, trees and hills were taken into consideration, as well as accessibility.

### D. Stack Testing Program

Coordinated with the ambient air monitoring program was a source testing program. The primary emission source on the SYNTHANE pilot plant site was the thermal oxidizer. At the initiation of the program, April 1977, all of process wastewater and gases generated by the plant were combusted in the thermal oxidizer. The source sampling served to measure the concentration of various pollutants emitted from this point source. Attempts were then made to compare this information with ambient pollutant concentrations as determined by the air monitoring network. The source sampling program also served to demonstrate compliance to source emission standards. The parameters measured were as follows:

### Elemental Analysis

Arsenic  
Beryllium  
Cadmium  
Fluorine  
Iron  
Lead  
Nickel  
Selenium  
Titanium

### Carbonyls

Nickel carbonyl  
Iron carbonyl

### Other Effluent Contaminants

SO<sub>2</sub>  
NO<sub>x</sub>  
H<sub>2</sub>S  
Organics  
Particulates

Sampling and analytical procedures are noted in Appendix B.

### Fugitive Emissions

The Fugitive Emissions Program was planned at the SYNTHANE pilot plant. An inventory had been performed in March, 1978 but no sampling had been undertaken due to the pilot plant operating schedule. Sources that were considered included: baghouse, char pond surface, oil water sump, decanter safety flare, high pressure valves, coal grinding vent system, slurry/filter feed tank, CO<sub>2</sub> vent, wastewater receiver tank vent and open top holding tanks. The actual sampling was expected to begin during the early months of 1979.

## II. Water Monitoring

The water monitoring program conducted at the SYNTHANE pilot plant consists of three phases--Surface Water Control, NPDES Sampling and Continuous Water Monitoring.

### Surface Water Control

The surface water control program was designed to minimize contamination of site effluent from spills and non-point source discharges. It has become an integral part of the Spill Control and Countermeasure Plan (SPCC), as well as the water pollution control program. Pilot plant operations are characterized by frequent maintenance procedures. This results in unusually high potential for spills to occur and debris to accumulate in process areas. These characteristics added to the inherent coal handling problems present a potentially significant surface water contamination problem. In an attempt to mitigate

pollutant loading in the plant effluent, paving and trenching of the process area was undertaken. The concrete paving was sloped to a trench and covered with an iron grill. The trenching carries the surface runoff to two holding tanks (15,000 gal each). The original plan was to collect the surface runoff in the tanks and upon accumulation to analyze the water. If the analysis fell within a specified range the water could be discharged as a batch process. The original plan also provided that during extended periods of rain the initial runoff could be collected in the holding tanks. After the runoff has been washed clean, a valve would redirect the water runoff directly to the storm sewer. As experienced at the pilot plant the effective execution of a surface water control program requires good housekeeping, strict control procedures and close surveillance to minimize the amount of contaminated runoff.

#### NPDES Sampling

The Code of Federal Regulations, Title 40, requires that owners or operators of a facility discharging via a point source must possess a National Pollutant Discharge and Elimination System (NPDES) permit. This NPDES permit includes effluent limitations to which the owner or operator must demonstrate compliance through a routine sampling and analysis program.

The SYNTHANE pilot plant was issued a NPDES permit, effective July 28, 1977, by the U.S. EPA. Recently the NPDES program has been reorganized whereby the administrative responsibilities are being assumed by the Commonwealth of Pennsylvania, Department of Environmental Resources. This change in administrative responsibility from federal to state levels has already evolved in most other states. The reorganization is expected to change some permit parameters. The permit currently contains discharge limitations for five effluent points. These include a sewage treatment plant, cooling tower blowdown, demineralizer, boiler blowdown (high and low pressure). These five discharge points have been determined to include all discharge contributions to the receiving stream. The justification for this decision was delineated in a December 4, 1975 memorandum to U.S. EPA. The EPA regional office agreed that the PETC proposed sampling sites were more feasible and representative than the single sampling point originally proposed by EPA.



The initial siting of the SYNTHANE pilot plant included the excavation of the valley in which the plant is situated which resulted in the diversion of the natural drainage through a 48" interceptor line, Figure 2. The pilot plant was then constructed over this interceptor along with a 15" storm drain and a 12" perforated drain. The five pilot plant discharge points (previously outlined in NPDES Section) contribute to these three underground drains and are subsequently mixed to form a single effluent stream in a 10' x 10' x 10' concrete box that is located (underground) at the eastern boundary of the pilot plant.

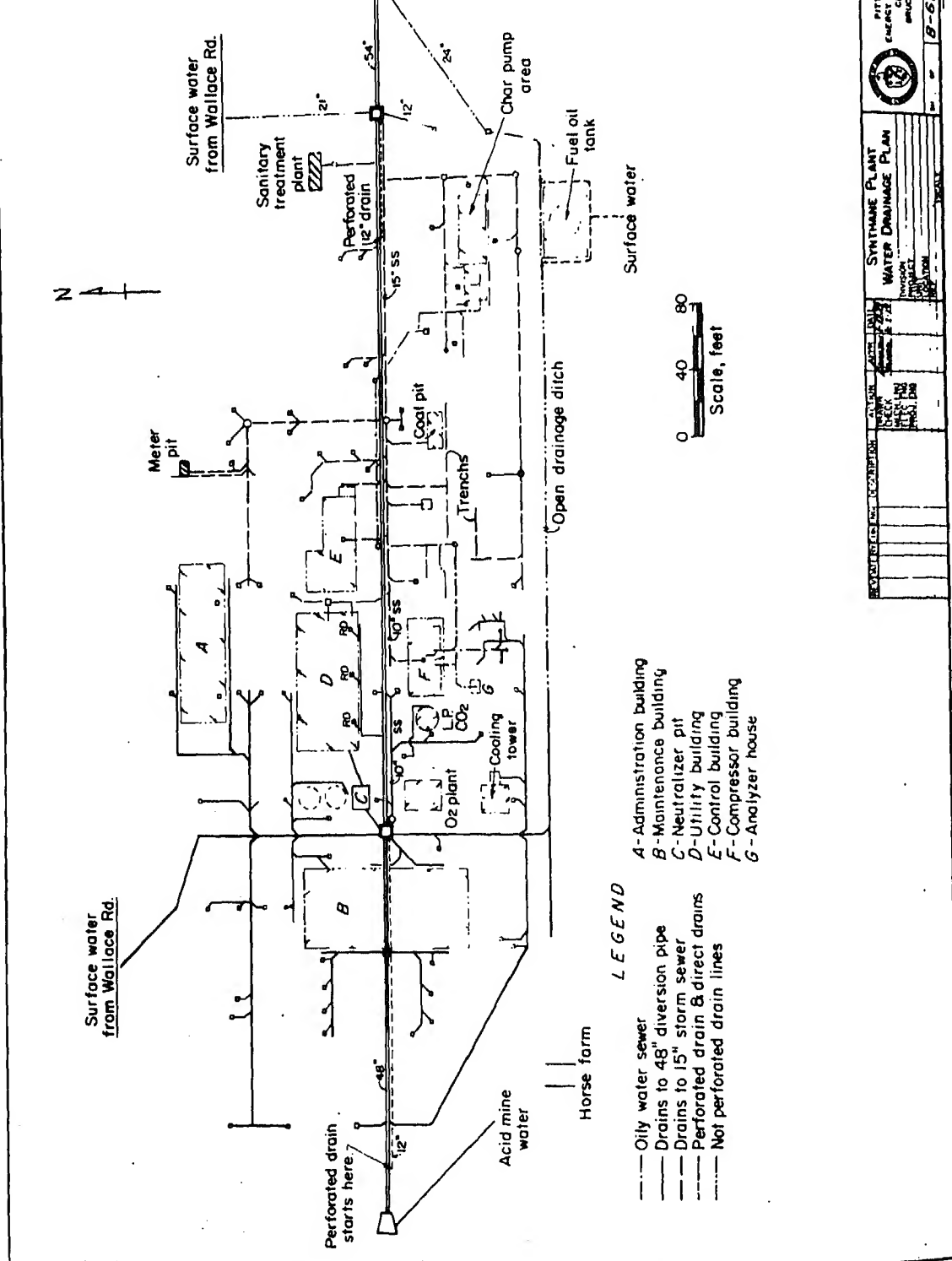
The approach taken to characterize the pilot plant contributions to the receiving stream includes five continuous water monitors, one at the plant inflow at the 48" line, one at the discharge end, one each at the 12" and 15" lines and one to measure the combined flow of the 10' x 10' x 10' concrete box. Flow measurements have been attempted at both inflow and outflow. At this time the "other sources" (storm drainage and road runoff problems) that have contributed to the total plant runoff are being separated out by a rerouting of surface water drainage lines. This source contribution has complicated sampling by blocking lines and interfering with flow measurements. Upon completion of this rerouting of storm drainage and road runoff the original continuous sampling schedule was to be resumed.

At the present time the continuous monitoring network consists of one 24-hour continuous sampler and flow meter at the plant inflow and three continuous samplers plus a flowmeter at the outfall. The samples are visually inspected and general pollutant analyses are performed if determined necessary. The analysis could be performed by the on site Lummus Lab or through a local university contract.

Parameters measured in the water monitoring program for most sampling points include: biological oxygen demand (BOD-5), fecal coliform, conductivity, oil and grease, phenol, pH,  $\text{NH}_3$ , suspended solids, total dissolved solids (TDS), chemical oxygen demand (COD) and iron.

### III. Noise

The noise monitoring program at the SYNTHANE pilot plant consisted of two phases: an ambient noise assessment and an inplant noise assessment.



A background noise assessment was conducted for the SYNTHANE pilot plant during September-October 1977. The concern in this program phase was strictly in regard to the noise emission from the plant rather than with respect to any of its operating characteristics. The principal noise producers in the plant were divided into the following categories:

Mechanical: grinders, pulverizers, gears, conveyors.

Flow Devices: fans, blowers, compressors, valves.

Combustion: furnaces, flares, heaters.

Electromechanical: generators, motors, transformers, circuit breakers.

Augmenting the operating noises were noises produced by maintenance operations and those resulting from truck movement.

A two-step approach was utilized in acquiring the needed data. The first step was field recording of the noise and the second was laboratory analysis of the recorded data.

The field recording system consisted of a sound level meter, a battery powered tape recorder, and an acoustic signal generator for providing the necessary reference signal. A windscreen was used over the input microphone to eliminate wind generated noise. Recordings were not made whenever the wind speed exceeded 15 miles per hour. The frequency response of the sound level meter was set in the A-weighting mode, as this practice will tend to reduce chances of either overloading the sound level meter or saturating the magnetic tape. The sound level meter also served as a calibrated attenuator for the tape recorder. On playback, the signal from the tape recording was fed through a calibrated attenuator into a level recorder. The signal coming out of the level recorder was then sorted by a distribution analyzer into various level intervals. A 5 dB interval was chosen for this study.

The tape recorder had a dynamic range of about 45 decibels. By appropriately adjusting the input level at the start of a recording session, overloading was never observed. The period of measurement spanned the better parts of September and October. The data were tabulated to enable any future correlation of the noise data with the plant operation log and other pertinent environmental data.

The data revealed that noise emission from the plant has a significant impact upon an area as far as about a mile to the east of the plant. It was also determined that a flare stack located atop the thermal oxidizer was a significant contributor of noise emissions. The flare subsequently was modified to reduce the venturi effect and the noise level was reduced to an acceptable level. This noise monitoring program has made it apparent that much lower noise levels are required in rural areas where ambient levels are generally low. The variability of noise level tolerances due to background levels should be an important consideration in siting plant operations.

#### In-Plant Noise Assessment

The in-plant phase of the noise monitoring program was planned and awaited resumption of the pilot plant operations. The initial monitoring and data collection was expected to begin in Fiscal Year 79. Equipment which was to be used in this study included: precision sound level meter with octave band analyzer; tape recorder, real time noise analyzer; and strip chart recorder. The in-plant noise assessment was to concentrate on the areas categorized in the ambient noise assessment section of this paper.

#### Occupational Health Program

Many of the occupational health programs for coal conversion processes have been based on the literature documenting hazards of coke oven emissions. Coke oven emissions and coal conversion emissions are considered by some experts to be similar in various categories. It is generally viewed by these health scientists that it would be prudent to develop model occupational health programs similar to those used in coke oven hygiene programs until a knowledge of the specific hazards can be discerned. The investigations to determine the specific worker health hazards of the SYNTHANE process have been underway. Included in these investigations were industrial hygiene type monitoring and biological laboratory testings. Until specific hazards and problem areas were known, protective clothing was worn by workmen who were exposed to potentially hazardous waste products and emissions.

operations were also considered for use or proposed in the SYNTHANE program.

The SYNTHANE pilot plant program was assessed in preparation of "Recommended Health and Safety Guidelines for Coal Gasification Pilot Plants", prepared by Enviro-Control for NIOSH.

### Solid Waste Program

The recent passage of the Toxic Substance Control Act (TSCA) and the Resource Conservation and Recovery Act (RCRA) has made it increasingly evident that more attention must be made to acceptable disposal and handling of solid wastes. The solid wastes program at the SYNTHANE pilot plant has accelerated in recent months. This acceleration included a project conducted by the EC Division, evaluates solid waste products for toxicity, leachability, mutagenicity and carcinogenicity. This is being conducted through carefully controlled laboratory studies. Leachate studies have been completed on specific waste products in the past. These studies indicated that char pond solids have the potential to create a leachate problem and require special handling. Studies have been conducted on the dewatered char from the SYNTHANE process. This char has been determined to cause no leachate problem and may be disposed of in conventional landfill operations. Data from biological testing concerning the mutagenicity of coal tar products from the SYNTHANE pilot plant process are expected shortly. These data will define parameters for more advanced toxicity testing to provide for environmentally sound disposal practices.

### SUMMARY

The U.S. Department of Energy (DOE), as part of our country's overall efforts to address and resolve energy issues, has engaged in a broad range of R&D activities. A major emphasis of these efforts has been focused on the utilization of coal as an energy source. Coal conversion technology is currently developing in several specific areas. The objective of this paper has been to discuss the environmental activities related to one specific coal conversion process referred to as the SYNTHANE Coal Gasification Process.

demonstration units. Consideration of problem areas identified at SYNTHANE will be useful as a preventive tool to be utilized in the design and implementation of these similar programs

Some highlighted considerations in conducting environmental assurance programs as identified through the SYNTHANE environmental efforts appear in Appendix C.

DOE has assumed the major responsibility for environmental health aspects of its technologies. This includes the evaluation and assessment of the environmental impact of each developing technology, such as SYNTHANE. The overall practicability and commercialization of these energy technologies depend heavily on their ability to comply with existing and future environmental/health regulations. It seems prudent to assess and develop simultaneously the environmental control technologies and process technology. The early incorporation of environmental concerns will serve to minimize the ultimate environmental impact and perhaps reduce or eliminate the expense of retrofitting control devices on the final process.

Sampling methods utilized in the mobile van data collection activity:

1.  $\text{SO}_2$  - one hour impinger samples at 840 cc/min. using West-Gaake Absorbing Reagent. Analysis was by colorimetry using pararose-aniline-formalhyde-Method B.

REF. Method 42401-01-69T - Intersociety Committee Methods of Air Sampling and Analysis.

2.  $\text{H}_2\text{S}$  - one hour impinger samples at 1.30 l/min. using cadmium hydroxide slurry as absorbing reagent. Analysis was by colorimetry of methylene blue produced by the reaction of sulfide with reagents.

REF. Method 42402-01-70T - Intersociety Committee Methods of Air Sampling and Analysis.

3. Phenol - one hour impinger samples at 1.85 l/min. using 5% sodium carbonate as absorbing reagent. Analysis was by colorimetry using 4-aminoantipyrine reagent.

REF. Standard Methods for Water and Waste Water Analysis, 13th. Edition.

4. Coefficient of Haze - Particulate was sampled using the AISI Paper tape sampler.

REF. ASTM D-1704-61 - Standard Method of Test for Particulate Matter in the Atmosphere.

Sources," except as follows:

1. Due to the high temperatures present in the thermal oxidizer stack, a water-cooled sampling probe was used. The portion of the probe not exposed to the high temperatures was heated to prevent condensation.
2. Due to difficulties encountered rigging the traditional probe/impinger box configuration, a heated teflon house was included to allow a flexible connection between the sampling probe and impinger box. The hose temperature was maintained at 250°F or greater to prevent condensation. Acetone washing from the hose was included with that of the probe.
3. Sampling for fluoride emissions (Method 13A) was combined with the particulate sample. A stainless steel screen filter support was used rather than a fitted glass type. The glass support has been shown to retain fluoride (Amendments to Reference Methods 13A and 13B, Federal Register, Vol. 41, No. 230, Nov. 29, 1976, Title 40, Part 60). Test methods and procedures for 13A and 13B appear in the Federal Register, Vol. 40, No. 152, Aug. 6, 1975.
4. The third impinger contained caustic, rather than being dry, to collect arsenic and to protect equipment from acid gases.

#### Metals

Arsenic, beryllium, cadmium, lead, and nickel contents of the particulate catch were determined by atomic absorption. Impingers 1, 2 were also ether-chloroform extracted to determine condensible organics.

#### NO<sub>x</sub>

U.S. EPA Method 7 was utilized. The sampling train equaled that of Figure 7-1 of the Method.

#### SO<sub>2</sub>, H<sub>2</sub>S

SO<sub>2</sub> by U.S. EPA Method 6 and H<sub>2</sub>S measurements were combined, according to the State of Texas procedure. The sampling train equaled that of the procedure except the glass fiber filter had to be omitted due to the high temperature. However, the catch was filtered using a glass fiber filter prior to analysis. A quartz sampling probe was substituted for the pyrex due to high temperatures.

Since the State of Pennsylvania requires a different SO<sub>2</sub> analysis, the sampling and analytical procedures followed the APCD, County of Los Angeles, Method for Oxides of Sulfur, page 85, Source Testing Manual, 1965. The in-stack thimble had to be omitted due to the high temperature, but the catch was filtered using a glass fiber filter prior to analysis.



as identified through the significant environmental efforts:

Proper segregation of contaminated wastewater from other aqueous effluents. This will facilitate optimum sampling accessibility and representativeness and minimize the volume of wastewater requiring treatment.

Precise documentation of operations schedules concerning air emissions. This documentation is necessary to correlate field ambient air monitoring with operations emissions to yield meaningful evaluations of various pollutant impacts from specific point sources.

Appropriate considerations of community noise levels in conducting the site selection process. Siting in the vicinity of a residence with conservative background noise levels has a much greater adverse impact than an area with higher community noise levels.

The types of solid waste generated by the plant should be considered in the siting process. Certain types of waste require special disposal techniques and facilities. The proximity of the appropriate disposal facilities is important due to high transportation costs and stringent DOT and EPA regulations.



Chairman: Stephen Freedman

Co-Chairman: Jerry Pell



by

J. S. Halow, U. Grimm, J. S. Mei

U.S. Department of Energy  
Morgantown Energy Technology Center

A program was initiated late last year at the Morgantown Energy Technology Center, Department of Energy to demonstrate a 90 percent sulfur retention capability in the 18-inch atmospheric fluidized-bed combustion (AFBC). This program was undertaken in response to concerns about the impact of possible New Source Performance Standards (NSPS) proposed by the Environmental Protection Agency in sulfur emissions. A high volatile bituminous coal with 4.42 percent of sulfur content was selected for this study. Greer limestone as well as tymochtee dolomite were used as bed material and sorbent. Combustion tests were carried out at various operating conditions to develop AFBC engineering and emissions data on this high sulfur coal. Ninety or greater percent of sulfur retention was attainable in several of the eighteen balance periods depending on operating conditions. The results of the present tests clearly demonstrate that the proposed new standards for sulfur dioxide emissions can be met by AFBC's. The required operating conditions could, however, have serious impact on AFBC economics.

#### GAS TURBINE CATALYTIC COMBUSTORS FOR COAL DERIVED FUELS

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U. S. Department of Energy  
Energy Technology

Catalytic combustion for gas turbines is a unique process which promises very low NO<sub>x</sub> emission levels at high efficiencies and comparable pressure drops. The Department of Energy (DOE) is expanding the catalytic work of EPA and NASA into the area of coal-derived fuels, both gases and liquids. On-going programs for the combustion of low Btu gas, medium Btu gas, and heavy liquids are described. Future plans for possible field tests are discussed.

U.S. Department of Energy

Grand Forks Energy Technology Center

The atmospheric fluidized-bed combustion of Western and Gulf Coast lignites and subbituminous coals offers a method of utilizing these low-sulfur, high-alkali coals with possibly little or no added sulfur sorbent. Tests using a 60inch atmospheric fluidized-bed combustor showed that eight of ten Western coals could be burned without addition of limestone and meet the standard of 1.2 lb  $\text{SO}_2$ /MM Btu. The downward revision in the NSPS will change the design criteria for these low-rank coals, as well as high-sulfur bituminous coals, but the sulfur retention on ash will still make a substantial contribution.

For the low-rank coals tested, the calcium-to-sulfur ratio ranged from 1 to over 4, and the sulfur retention from nearly 0 to over 90 pct. Reinjection of primary cyclone fly ash increased sulfur capture significantly, but not sufficiently to insure compliance of all low-rank coals under the NSPS standards. Bed temperature influenced sulfur retention in the range of 1250° to 1600°F, with maximum retention at 1400°F without ash reinjection and 1500°F with ash reinjection. During operation some of the coal ash agglomerated within the bed and was also deposited on the tube walls.

Tests for characterizing gaseous and particulate emissions from the AFBC have been performed; preliminary results of these tests are presented in this paper. The physical and chemical characteristics of the fly ash produced in the AFBC with and without cyclone ash recycle are examined.

CONTROL OF NITROGEN OXIDE EMISSIONS IN  
COAL-FIRED, OPEN-CYCLE MHD POWER PLANTS

Joseph Epstein

U. S. Department of Energy

Energy Technology

The control of nitrogen oxide ( $\text{NO}_x$ ) emissions from coal-fired powerplants, including Magnetohydrodynamic (MHD) systems is an issue which most often appears in the evaluation of a new technology. Since the 1960's, the MHD community has given considerable attention

Present information indicates that both current and future NO<sub>x</sub> standards can be met by the MHD process even though no credit is provided for the significant increase in net plant efficiency over conventional power-plant systems.

Presently available results from experiments as high as 8 Mwt and from calculations based on experimentally derived kinetics data have served to empirically identify realistic NO<sub>x</sub> control techniques. The preferred system operation is to: (a) operate the coal combustor fuel rich, (b) cool the gas slowly in a radiant boiler downstream of the MHD channel/diffuser, (the radiant boiler is the key component in MHD NO<sub>x</sub> control), and (c) add additional air to the radiant-boiler exhaust, at a temperature high enough to complete combustion but, low enough to minimize the tendency to form additional NO<sub>x</sub>. These concepts are discussed in detail along with experimental and analytical results that have been obtained to verify that the method of control is technically sound and practical. Current DOE-sponsored R&D efforts are aimed at optimizing the method and at formal demonstration in suitable facilities.

#### CONTROL OF SULFUR DIOXIDE AND PARTICULATE EMISSION IN MHD POWER SYSTEMS USING HIGH SULFUR COAL

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MHD power generation systems offer an attractive opportunity to utilize high sulfur coal and yet reduce the emissions of sulfur oxides as well as the oxides of nitrogen and particulate matter. Interaction of sulfur compounds with the potassium seed material added to the coal or combustion products to make the MHD process work results in an attendant reduction of SO<sub>2</sub> emissions of 80 to 90 percent. The sulfur compounds released in the combustion of coal interact with potassium forming solid potassium sulfate. The potassium must be recovered in an MHD system and reprocessed in order to

the interaction of potassium compounds. These results are compared with available experimental information, which summarizes the effectiveness in which  $\text{SO}_2$  emissions are compared to present EPA standards, as well as anticipated emission standards for  $\text{SO}_2$  in the future. Finally, some comments are made as to the applicability of this control measure as a retrofit means to control  $\text{SO}_2$  emissions in existing utility boilers.

## FLUE GAS CLEANING FOR PRESSURIZED FLUIDIZED-BED COMBUSTORS

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Studies underway at ANL to clean up the hot flue gas from a PFBC so that it will be suitable for gas turbine use will be reviewed. Granular limestone beds and high efficiency cyclones are under study for particulate removal. Acoustical preconditioning of the flue gas is being evaluated as a method to increase the particulate size in order to increase the efficiency of cyclones. Two laser on-line particle size and concentration analyzers have been experimentally evaluated. The use of hot granular bed filters for the removal of gaseous alkali metal compounds is under study. Two sorbents, diatomaceous earth and activated bauxite, have been found to be highly effective for the removal of gaseous  $\text{NaCl}$  and  $\text{KCl}$  from hot flue gas.

## REDUCING THE ENVIRONMENTAL IMPACT OF SOLID WASTES FROM A FLUIDIZED-BED COMBUSTOR

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The effectiveness of three options for the reduction of the environmental impact of solid sorbents used to control the  $\text{SO}_2$  emission from fluidized-bed coal combustion systems will be compared. These options are: (1) pretreatment of the sorbent (use of chemical additives such as  $\text{NaCl}$  or  $\text{CaCl}_2$ ) to increase its reactivity with  $\text{SO}_2$ , (2) regeneration and reuse of the sorbent, and (3) the use of synthetic sorbents. The quantity of waste generated decreases in the order (1) to (3); the cost increases in the order (1) to (3). The use of chemical additives and the regeneration and reuse of the limestone are viable options. The high cost of synthetic sorbents currently available rule out this option from further consideration.



by

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#### ABSTRACT

A program was initiated late last year at the Morgantown Energy Technology Center, Department of Energy to demonstrate a 90 percent sulfur retention capability of an atmospheric fluidized-bed combustor (AFBC) burning a high sulfur coal. This program was undertaken in response to concerns about the impact of possible New Source Performance Standards (NSPS) proposed by the Environmental Protection Agency on the application of AFBC technology. A high volatile bituminous coal with 4.42 percent sulfur content was selected for this study. Greer limestone as well as Tymochtee dolomite were used as sulfur sorbents. Combustion tests were carried out at various operating conditions to develop AFBC engineering and emissions data on this high sulfur coal. Ninety or greater percent of sulfur retention was attained in nine of the nineteen balance periods. Eighty-five or greater percent sulfur retention was attained in fourteen of the nineteen balance periods. The results of the present tests clearly demonstrate that the proposed new standards for sulfur dioxide emissions can be met by AFBC's.

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Fluidized-bed combustion of coal is a process that has been under study since the early 1960's in both England and the United States. This process offers a means of burning a variety of coals and other fuels in an environmentally acceptable manner.

In a fluidized-bed combustor, coal is burned in a bed of inert ash and limestone or dolomite fluidized by the injection of air through the bottom of the bed at controlled rates. The limestone or dolomite in the bed reacts with the sulfur dioxide released by the combustion of the coal, and forms a solid sulfate. Heat is extracted by tubes immersed in the bed and above the bed. Advantages of the AFBC include: Early commercial availability, a projected competitive cost, controllable emissions of  $\text{SO}_x$  and  $\text{NO}_x$ , fuel flexibility, and a solid spent sorbent stream that can readily be disposed of along with the coal ash.

At present, New Source Performance Standards (NSPS) limits sulfur dioxide ( $\text{SO}_2$ ), nitrogen oxides ( $\text{NO}_x$ ), and particulate matter that can be emitted from a utility boiler stack. Suppression of  $\text{SO}_2$  and  $\text{NO}_x$  in a fluidized-bed boiler is achieved in the combustion process. The combustion stability provided by the fluidized bed and the balance of heat input and removal from the bed maintains combustion at temperatures below the ash fusion point, and low enough to permit the conversion of limestone and  $\text{SO}_2$  to sulfate and to inhibit the formation of nitrogen oxides. To meet NSPS for particulates, conventional mechanical collector and dust removal precipitators or filters will likely be adequate.

This paper discusses  $\text{SO}_2$  capture in an AFBC when burning high sulfur coals. Experimental tests burning a high sulfur bituminous coal were conducted in the Morgantown Energy Technology Center's 18-inch diameter combustor. This study was undertaken in response to concerns about the impacts of proposed New Source Performance Standards on AFBC technology.

### Variables Effecting Sulfur Capture

Sulfur capture is dependent on a number of design and operating variables as well as the sorbent used. A primary variable which can be readily controlled is the calcium to sulfur mole ratio. Increasing the Ca/S mole ratio increases the amount of active sorbent in the bed, thereby increasing sulfur capture. Also of importance is the bed temperature since the  $\text{SO}_2$ /sorbent reaction is temperature dependent. An optimum sulfur capture temperature of around 1550°F is common for many sorbents. In designing and operating AFBC's, it is desirable to minimize Ca/S mole ratio since high sorbent usage significantly impacts AFBC economics through the cost of sorbent, parasitic heat losses through calcination, and increased spent sorbent disposal costs.

time with the sorbent, also increases gas residence time and, therefore, increases sulfur capture. These variables along with the Ca/S mole ratio need to be balanced to achieve efficient sulfur capture with an economically viable design. Sorbent variety also has a significant effect on sulfur capture.

Reported pilot plant data (1,2,3) has shown sulfur retention results of 90 percent or greater on a variety of fuels and sorbents. Test results reported in this paper provide additional data. Also, since the tests were performed to specifically meet high sulfur capture conditions, the current data allow correlation with operating variables.

#### Characteristics of Fuel and Sorbents Used in Tests

The coal used in this investigation was a bituminous-A, high volatile coal with a sulfur content of 4.42 percent. It's origin was the Pittsview Coal Company in National, WV, approximately 5 miles south of Morgantown, WV. The company is mining a coal formation better known as the Sweeney seam. The chemical analysis of this coal is given in Table 1.

Table 1  
Composition of Pittsview Coal

Moisture %	0.94	Ash analysis %	
Ash %	14.04	SiO <sub>2</sub>	44.90
Sulfur % Total	4.42	Al <sub>2</sub> O <sub>3</sub>	22.91
Pyritic	2.36	Fe <sub>2</sub> O <sub>3</sub>	22.71
Hydrogen %	5.18	CaO	1.06
Total Carbon %	69.45	MgO	0.82
Nitrogen %	1.15	Na <sub>2</sub> O	0.28
Oxygen %	4.85	K <sub>2</sub> O	2.08
		P <sub>2</sub> O <sub>5</sub>	0.07
Btu/lb	12,700	TiO <sub>2</sub>	1.18
		SO <sub>3</sub>	1.00

Table 2  
Screen Analysis of Coal

<u>Size Range</u>	<u>1/4 x 0, %</u>	<u>1/8 x 0, %</u>
1/4"-4 mesh	8.1	0.2
4-8 mesh	37.9	8.8
8-16 mesh	21.9	20.7
16-30 mesh	13.5	25.5
30-50 mesh	6.9	17.8
50-100 mesh	3.9	12.1
100-200 mesh	3.0	8.2
200-	4.8	6.8

The sorbents used in the test program were Greer limestone and Tymochtee dolomite. Greer limestone is the predominant limestone in the area of West Virginia's high sulfur coals and its sorbtion characteristics can be classified as good to very good. Tymochtee dolomite was chosen because thermogravimetric analyzer (TGA) studies by the Argonne National Laboratory have classified this material as one of the best sorbents. It originated in Huntsville, Ohio, a dolomite formation approximately 50 miles northwest of Columbus, Ohio. The chemical analysis of both materials are listed in Table 3. The sorbents were air dried, crushed, and screened before being fed to the FBC at the top of the expanded bed. The size distributions of sorbents used in the tests are presented in Table 4.

Table 3  
Composition of Sorbents

<u>Elemental Analysis</u>	<u>Tymochtee Dolomite</u>	<u>Greer Limestone</u>
As Carbonates*		
CaCO <sub>3</sub> %	53.88	86.2
MgCO <sub>3</sub> %	41.49	5.34
As Oxides*		
CaO%	28.04	44.8
MgO%	19.84	2.15
CO <sub>2</sub> %	42.05	47.37

\* Balance is moisture, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and traces.

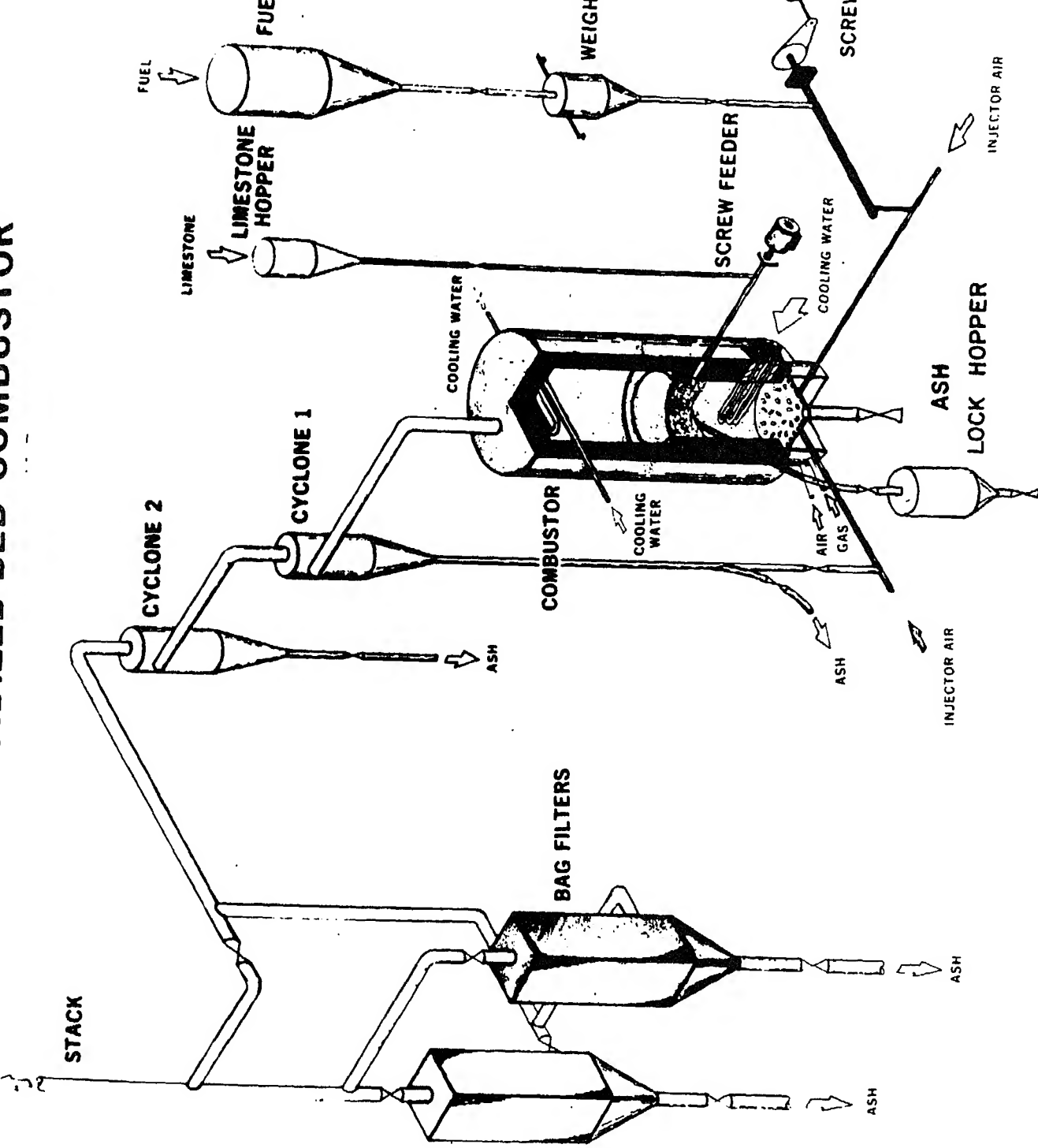
Size Range	Greer Limestone Wt %		Tymochtee Dolomite Wt%	
	1/4 x 10 mesh	1/4 x 30 mesh	1/4 x 28 mesh	5/10 x 3/32
1/4"-4 mesh	39.8	2.28	0.2	47.87
4-6 mesh	49.9	--	--	--
4-8 mesh	--	34.8	27.7	49.40
6-10 mesh	9.7	--	--	--
8-16 mesh	--	30.34	20.4	1.53
10-12 mesh	0.4	--	--	--
16-30 mesh	--	14.61	17.8	.08
30-50 mesh	--	5.32	10.1	.16
50-100 mesh	--	4.03	6.4	.08
-100	--	8.59	17.4	.88

#### EXPERIMENTAL FACILITY AND START UP PROCEDURE

The experimental facility at the Morgantown Energy Technology Center for fluidized-bed combustion of low-quality fuel feasibility studies is shown schematically in Figure 1. It is basically a refractory-lined cylindrical combustor having an internal diameter of 0.46 m (18 inches) in the 1.14 m (45 inches) high bed region with an attached 0.69 m (27 inches) high expanded freeboard section of 0.61 m (24 inches) diameter.

The combustor contains a set of hair-pin-type water cooled heat exchanger tubes located in the bed region and a single pass water cooled heat exchanger in the expanded freeboard. Coal is metered from a hopper and is fed into a fuel injection chamber by a screw feeder. The coal is then injected into the bed near the base of the conical air distributor plate by compressed air. Limestone, when used, is metered from a hopper and fed by a screw feeder directly into the top of the expanded bed. Entrained particulates in the flue gas leaving the combustor are removed by two stages of cyclones followed by bag filters. Particulate matter removed by the primary cyclone is reinjected into the bed for additional carbon burnup. Flue gas leaving the combustor is continuously sampled and analyzed. CO and CO<sub>2</sub> are determined by non-dispersive infra-red analyzers. A chemiluminescence analyzer is used to determine NO and NO<sub>x</sub>. SO<sub>2</sub> and total hydrocarbon analyses are made by a flame photometric analyzer and a flame ionization analyzer, respectively, and O<sub>2</sub> by a paramagnetic analyzer.

Start up of the unit is accomplished by preheating the lower part of the combustor to 816°C (1500°F) with premixed natural gas and air. When the desired temperature level is reached, approximately 23 kg (50 lb) of bed



gas is shut off. After a minimum sorbent addition until sulfur dioxide is seen in the flue gas. Then desired operating conditions are established and the unit allowed to stabilize before a data-taking balance period is started. Typical balance periods are 10 hours in duration.

## RESULTS OF SULFUR RETENTION STUDIES

It has been mentioned previously that the present study was undertaken in response to the concern about the impact of the proposed NSPS of 90 percent sulfur retention on AFBC technology. The studies, therefore, were carried out at conditions which could lead to high sulfur retention in the bed. The variables investigated for the present study have been Ca/S mole ratio, fluidized-bed temperature, gas residence time, type and particle size of sorbent. Table 5 presents a summary of the experimental conditions and the sulfur retention results for the experiments carried out in this study. The analysis of the results are discussed below.

Figure 2 illustrates the effect of average bed temperature on the percentage of sulfur captured by two different types of sorbent, Greer limestone and Tymochtee dolomite. Data for Greer Limestone show a clear temperature dependence (solid curve) in spite of variations Ca/S ratio, gas residence time and sorbent particle size. A maximum reactivity around 1550°F is evident. Tymochtee Dolomite does not show a clear trend in this data. An optimum temperature range for sulfur capture is observed for Greer limestone between 1500° to 1600°F. As seen, 90 percent or better sulfur retention can be obtained over the optimum temperature range.

The effect of Ca/S mole ratio on sulfur retention is shown in Figure 3 for the two sorbents at a bed temperature range between 1500° to 1600°F where sulfur capture had been optimized. The present results indicate that for this particular high sulfur coal and Greer limestone, a calcium-to-sulfur mole ratio of 2.0 would be adequate to assure compliance with the proposed NSPS of 90 percent sulfur removal. With Tymochtee Dolomite, a Ca/S ratio of 1.5 appears to be adequate to meet a 90% sulfur retention with the revised NSPS of 85 percent sulfur retention, lower Ca/S ratios would appear to be sufficient in the optimum bed temperature range and with the 0.75 sec to 1.00 sec residence times used in these tests, but the data is insufficient to draw a firm conclusion at this retention level. The calcium-to-sulfur ratio required to maintain 90 percent sulfur removal, however, is lower than the projected value ( $\text{Ca/S} \cong 2.8$ ) by Westinghouse kinetic model (4) and by the MIT model ( $\text{Ca/S} \cong 3.1$ ) (5) at similar operating conditions.



TABLE 5. SUMMARY OF EXPERIMENTAL CONDITIONS AND SULFUR RETENTION RESULTS

Run No.	Sorbent Type	Particle Size (Sorbent)	Particle Size (Coal)	Bed Temp. (°F)	Superfic. Velocity (ft/sec)	Bed Depth (ft)	Resid. Time (sec)	Co/S Mole (ratio)	SO <sub>2</sub> Emission (ppm)	SO <sub>2</sub> Emission (lb/10 <sup>6</sup> Btu)	Subst. Det.
1/1	G. Lime.	1/4"x10 mesh	1/4"x0"	1524	2.99	3.00	1.00	3.91	240	0.54	9
1/2	G. Lime.	1/4"x30 mesh	1/4"x0"	1470	2.91	3.00	1.03	2.62	646	1.42	8
1/3	G. Lime.	1/4"x30 mesh	1/4"x0"	1533	3.03	3.00	0.99	3.44	255	0.62	9
1/4	G. Lime.	1/4"x30 mesh	1/4"x0"	1536	3.45	3.00	0.87	2.05	259	0.63	9
1/5	G. Lime.	1/4"x10 mesh	1/4"x0"	1582	3.51	3.00	0.85	1.82	344	0.56	9
1/6	T. Dolom.	1/4"x28 mesh	1/4"x0"	1465	3.43	3.00	0.87	1.21	900	1.67	7
1/7	T. Dolom.	1/4"x28 mesh	1/4"x0"	1444	3.39	3.00	0.88	1.24	300	0.59	9
1/8	T. Dolom.	1/4"x28 mesh	1/8"x0"	1546	3.51	3.00	0.85	0.80	855	1.44	8
1/9	T. Dolom.	5/16"x3/32"	1/8"x0"	1547	3.51	3.00	0.85	1.20	412	0.75	8
1/10	T. Dolom.	5/16"x3/32"	1/8"x0"	1556	3.82	3.00	0.79	1.43	439	0.96	8
1/11	T. Dolom.	5/16"x3/32"	1/8"x0"	1554	3.95	3.00	0.76	1.44	303	0.57	8
2/1	G. Lime.	1/4"x10 mesh	1/4"x0"	1653	3.51	3.00	0.85	2.67	414	0.76	8
2/2	G. Lime.	1/4"x10 mesh	1/4"x0"	1507	3.27	3.00	0.92	1.87	112	0.19	9
2/3	G. Lime.	1/4"x10 mesh	1/4"x0"	1463	3.13	3.00	0.96	2.13	1427	2.78	6
2/4	G. Lime.	1/4"x10 mesh	1/4"x0"	1670	3.50	3.00	0.86	2.82	493	0.88	8
2/4R	G. Lime.	1/4"x10 mesh	1/4"x0"	1637	3.58	3.00	0.84	2.68	650	1.10	8
2/5	G. Lime.	1/4"x10 mesh	1/4"x0"	1555	3.44	3.00	0.87	2.99	155	0.31	9
2/6	G. Lime.	1/4"x10 mesh	1/4"x0"	1482	3.30	3.00	0.91	4.21	471	1.03	8
2/7	G. Lime.	1/4"x10 mesh	1/4"x0"	1562	3.42	3.00	0.88	3.91	152	0.39	9

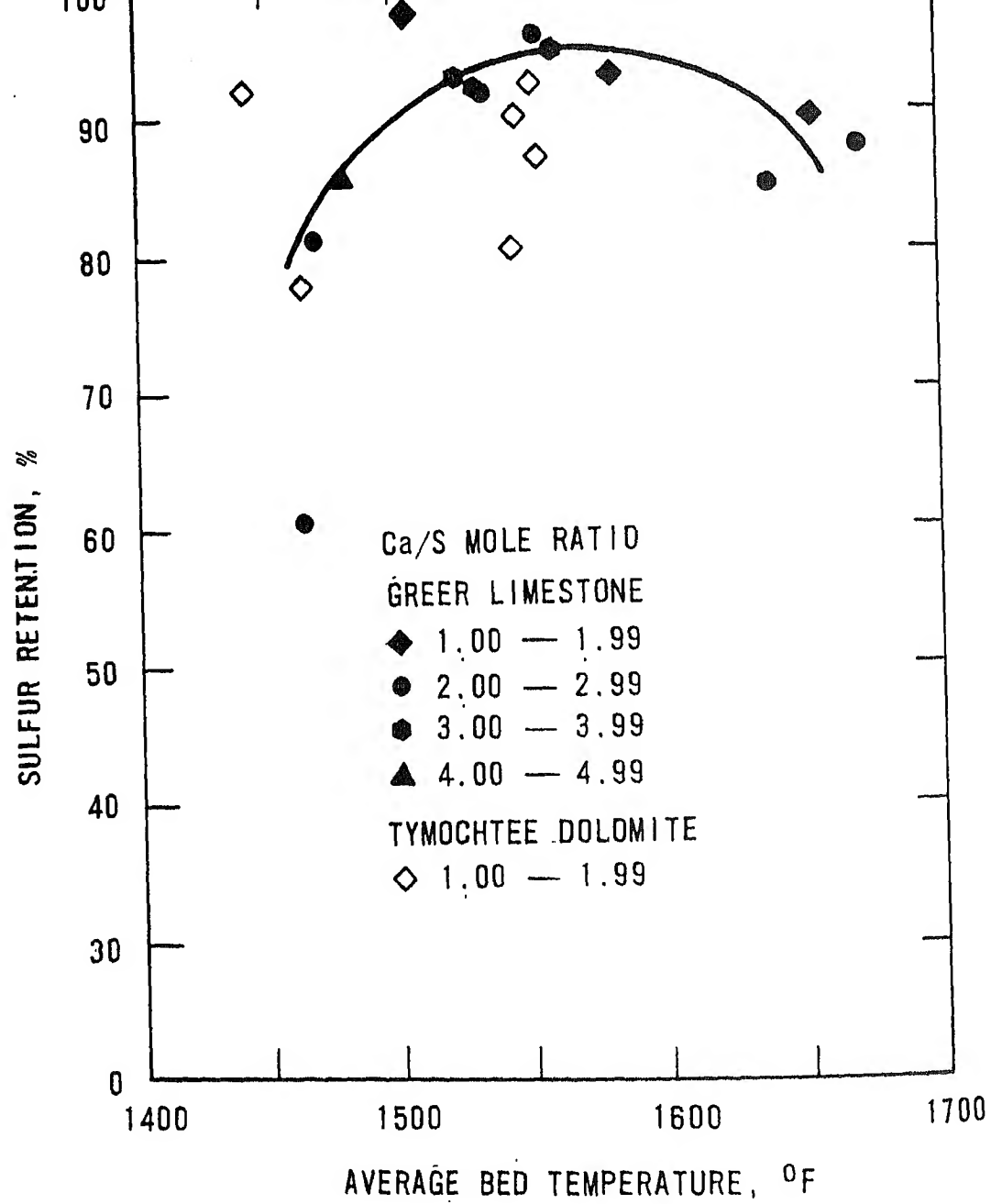


FIGURE 2. Effect of Average Bed Temperature on Sulfur Retention

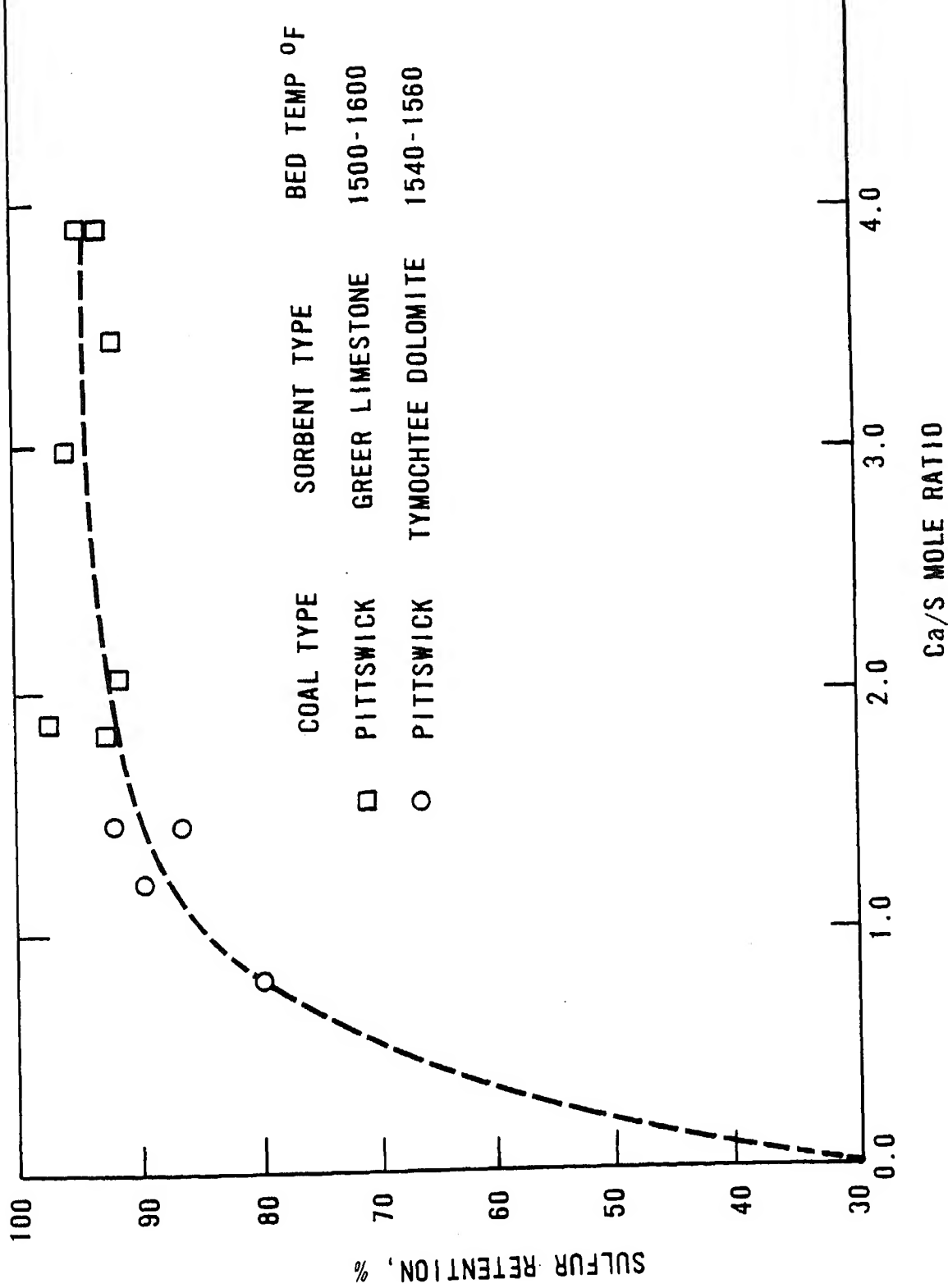


FIGURE 3. Effect of Ca/S Mole Ratio on Sulfur Retention